MANUFACTURE OF
ALUM & THE SULPHATES
OF ALUMINA & IRON

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THE MANUFACTURE OF ALUM

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THE

MANUFACTURE OF ALUM

AND THE SULPHATES AND OTHER SALTS OF ALUMINA AND IRON

THEIR USES AND APPLICATIONS AS MORDANTS IN DYEING AND CALICO PRINTING, AND THEIR OTHER APPLICATIONS IN THE ARTS, MANUFACTURES, SANITARY ENGINEERING, AGRICULTURE, AND HORTICULTURE

164614

BY

LUCIEN GESCHWIND

TRANSLATED FROM THE FRENCH BY CHAS. SALTER

WITH 195 ILLUSTRATIONS

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INTRODUCTION

In compiling the present work, the author has endeavoured to collect the somewhat scanty literary data available on the manufacture of the sulphates of alumina and iron, and combine with them the results of his own researches, in order to bring before the reader a complete account of the processes involved in the treatment of the raw materials employed, namely, bauxite, alunite, pyritic lignites; and of the various applications of the resulting products.

The work has been divided into four parts:—

1. *A Theoretical Study of Iron, Aluminium, and their Compounds*, chiefly confining the question to the sulphates and the minerals employed in the operations described in the succeeding parts of the book. This section, it is hoped, will save the chemist and manufacturer the considerable trouble often encountered in seeking for information on theoretical points connected with practical procedure; and, furthermore, simplifies the subsequent sections, in so far as the reader is instructed beforehand in the composition and origin of the minerals, the reactions employed, and the characteristics (specific gravity, solubility, etc.) of the substances used.

2. *Manufacture of the Sulphates of Aluminium and Iron.* Here will be found a description of the various methods of manufacturing aluminium sulphate, the various alums, normal ferrous and ferric sulphate, and the basic ferric sulphates, more especially *Rouil* mordant. Wherever feasible, the costs of production have been given in detail, and possible improvements in the methods of manufacture have been suggested. A number of the illustra-

tions used are reduced from original drawings made on the spot, or lent by the proprietors of the works described.

3. *Applications of the Sulphates of Aluminium and Iron.* In this section an attempt has been made to go beyond a mere arid recapitulation of the uses to which these bodies are put, and to describe the mode of their employment, in order to save the reader the trouble of further research.

4. *The Analysis of the Iron and Aluminium Compounds*; this part containing, in addition to the usual tests, examples of the methods of analysing the natural and industrial products, such as bauxite, aluminium sulphate, aluminium hydroxide, etc.

The work is designed to meet the requirements of chemical manufacturers, chemical engineers, works managers, and others engaged in the various chemical industries producing or using alum, aluminium sulphate, the sulphates of iron, etc.

The author wishes to express his thanks to the following gentlemen, who have afforded great assistance in the fulfilment of his task — Messrs. Lacarrière (chemical manufacturer, Noyon), Vivien (St. Quentin), Bernier (Chailvet), Gaillot (Laon Agricultural Station), and Professor Hermant of the Institut Industriel du Nord, their advice and information having proved of great utility.

L. GESCHWIND.

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CHAPTER I

ALUMINIUM AND ITS COMPOUNDS

§ 1. ALUMINIUM (Al = 27)

1. **Preparation in the Laboratory.**—HISTORICAL.—Aluminium may be prepared in a perfectly pure state in the laboratory by reacting on purified aluminium bromide with sodium in a brasqued crucible. Another method is by heating alumina in presence of borax, carbon, and a little silica, the alumina being reduced to the metallic state.

The discovery of this metal is generally ascribed to Wöhler, this renowned chemist having prepared it, in 1827, as an impure grey powder, by decomposing aluminium chloride with potassium. Various ancient authors, however,—Petronius Arbiter (*Satyricon*, chap. li.), Dio Cassius (*R.R.*, lib. lvii. c. xxi.), Pliny (*Hist. naturalis*, l. xxxvi. c. lxvi. § 195),—mention a workman who discovered a method of separating from aluminous glass a new metal out of which he fashioned a cup which he presented to the Emperor Tiberius. In view of the well-known abundance of boric acid springs in Italy, it is not impossible that the method consisted in the employment of boric acid, potash, silica, and carbon, aluminium being formed as mentioned above.

The discovery of aluminium would thus appear to date back to a much earlier period than is generally believed. (See paper by Duboin, *Rev. gén. des Sciences*, Vol. 9, No. 16, p. 635.) The credit of having isolated the metal in a pure state and described its properties belongs to H. St. Claire Deville (1854); and, not satisfied with this result, the same chemist, after experimenting largely in collaboration with H. Debray and P. Morin, very soon afterwards founded the first industrial process for the manufacture of aluminium, at the works of Messrs. Rousseau frères at La Glacière.

This process, which at the present time is merely of historical interest, consisted in allowing slightly heated sodium to react on the vapour of aluminium chloride. Owing to the numerous difficulties encountered, the inventors had to modify their original plan by replacing the highly deliquescent aluminium chloride by the double chloride of aluminium and sodium. A fluoride was afterwards added to serve as a flux, the following proportions being taken:—

Sodium-aluminium chloride	400 grams.
Common salt	200 ,,
Cryolite	200 ,,
Sodium	75 ,,

This mixture, fused at a high temperature in a crucible provided with an aluminous brasque, yielded aluminium of fairly good quality.

2. **Preparation of Aluminium on a manufacturing scale.**—*A*. Chemical Methods.—At the present time the metallurgy of aluminium comprises two principal divisions: chemical and electrical methods. The former includes several processes, all more or less derived from the classic method of St. Claire Deville, the most important being

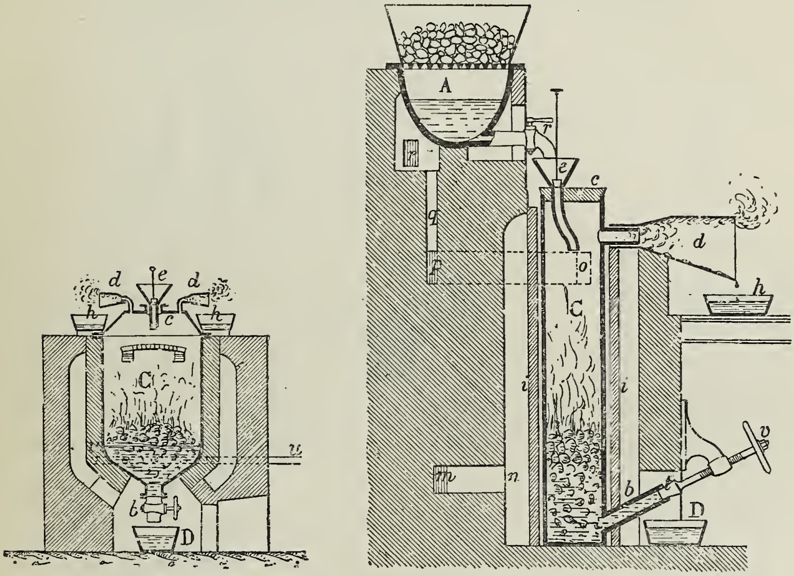
The Castner process, worked at Oldbury, near Birmingham;
The Netto process, worked by "The Alliance Aluminium Co." at Wallsend-on-Tyne, near Newcastle;
The Grabau process.

I. *The Castner process*.—The principal advantages of this process reside in the manner of preparing the sodium. Instead of employing sodium carbonate, which requires a very high temperature for its decomposition, caustic soda is used, this body decomposing at about 800° C., according to the equation

$$6NaOH + C_2 = 2Na_2CO_3 + 3H_2 + Na_2.$$

The carbon is introduced in the form of specially prepared iron carbide.

The double chloride is obtained by treating with chlorine a mixture of alumina, common salt, and carbon in horizontal retorts about 12 feet long, heated by gas. The double chloride is mixed with cryolite and the necessary quantity of sodium in a revolving cylinder, the whole being then rapidly transferred to a reverberatory gas furnace heated to the requisite degree for the performance of the reaction.



FIGS. 1 and 2.—The Netto process.

A, Caustic soda reservoir; *r*, tap for emptying same; *e*, funnel inlet for caustic soda; *c*, cover; C, reducing furnace; *t*, stopper, worked by wheel *v*; *i*, clay jacket; *d*, condenser for metallic sodium; *h*, oil reservoir; D, storage for residual Na_2CO_3; *b*, effluent pipe; *u*, tuyères; *m*, *n*, *o*, *p*, *q*, flues.

The quantities employed for a charge are: 1210 lbs. of double chloride, purified by fusion with a little powdered aluminium or sodium; 605 lbs. of cryolite, and 149·6 lbs. of sodium.

A fairly pure metallic aluminium is obtained.

II. *The Netto process.*—In this case the raw material consists of the double fluoride (cryolite) of aluminium and sodium, instead of the double chloride of these metals. In preparing the cryolite the inventor utilises the scoria resulting from the treatment of this salt with sodium, and consisting mainly of sodium fluoride. With this object he fuses the said residue with aluminium sulphate, and extracts sodium sulphate from the mass by lixiviation, leaving the insoluble double fluoride behind. The reaction is expressed by the equation

$$Al_2(SO_4)_3 + 12NaF = Al_2F_6, 6NaF + 3Na_2SO_4.$$

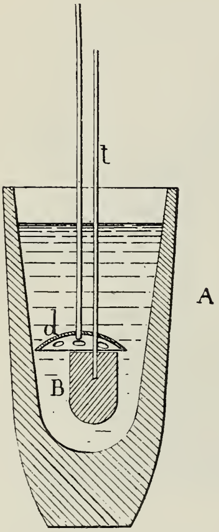


Fig. 3.—Introducing the sodium into the cryolite.

A, Crucible; B, block of sodium suspended from the rod *t*; *d*, perforated plug.

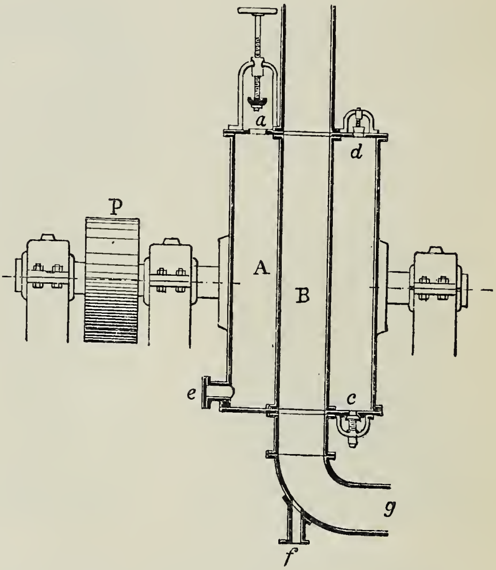


Fig. 4.—Converter for producing aluminium by the action of sodium on cryolite.

A, Reducing crucible; *a*, charging aperture; B, heating flue; *g*, pipe from gas furnace; *f*, air inlet; P, driving pulley; *e*, outlet.

The natural Greenland cryolite could of course be used, were it not rendered too expensive by the high rates of freight and by the monopoly established by the American owners of the deposits.

The object of the Netto method of preparing the sodium is to reduce to a minimum the formation of sodium carbonate, to carry out the reaction at a temperature low enough to permit the use of cast-iron retorts, and to separate immediately the sodium and sodium carbonate formed.

For this purpose the caustic soda is fed gradually to the glowing carbon ; the resulting vapour of sodium escapes as soon as formed and condenses in a lateral pipe situated at the top of the retort, whilst the sodium carbonate runs away uninterruptedly at the bottom (Figs. 1 and 2).

The operation is conducted at a bright red heat. One of the conditions essential to the success of the sodium treatment has been elucidated by Netto and Grabau, and that is, not to leave the sodium in contact with the cryolite any longer than is absolutely necessary. The arrangement employed by Netto is designed with a view to effect the immediate reaction of the sodium on the double fluoride.

The cryolite and the necessary amount of sodium chloride are fused at red heat in a refractory crucible. As soon as the mass is in a molten condition a block of sodium is introduced by means of a plug and a rod (Fig. 3), on which it has previously been moulded, whereupon the reaction is almost instantaneous. The apparatus is then tipped so as to discharge the contents into a cast-iron mould, from which, when cold, the aluminium is taken out as a solid block. The operation may also be performed in an apparatus analogous to the Bessemer converter (Fig. 4). The aluminium obtained is of a high degree of purity.

III. *The Grabau process.*—In this method metallic sodium is employed to reduce aluminium fluoride, the two being heated separately in order to obviate the great inconvenience arising from the corrosion of the vessels by fluorides. The aluminium fluoride, which is infusible at the temperature of the operation, is reduced to powder, and in this condition is brought into contact with the sodium. The reaction is expressed by the equation

$$2Al_2F_6 + 6Na = 2Al + Al_2F_6, 6NaF,$$

the cryolite, produced as a residue, tending to solidify on the walls of the crucible and protect them against the action of the mass.

Grabau prepares his aluminium fluoride by reacting with fluor spar on aluminium sulphate, the products being aluminium fluosilicate and calcium sulphate, according to the equation

$$Al_2(SO_4)_3 + 2CaF_2 = Al_2F_4SO_4 + 2CaSO_4.$$

The fluosilicate is then treated with cryolite—

$$3Al_2F_4SO_4 + Al_2F_6, 6NaF = 4Al_2F_6 + 3Na_2SO_4.$$

B. ELECTRICAL METHODS.—I. *The Cowles process.*—A mixture of alumina and carbon, with the metal destined to form an alloy with the aluminium, is introduced into an apparatus arranged in a similar manner to the Siemens crucible (Figs. 5 and 6). Under the influence of a powerful electric current the carbon reduces the alumina and liberates aluminium, which immediately forms an alloy with the metal introduced for that purpose. It would appear that the thermal effect of the current alone comes into play in this process, and a trial made with an alternating current machine gave the same yield of aluminium, in the condition of bronze, as was obtained by a continuous current.

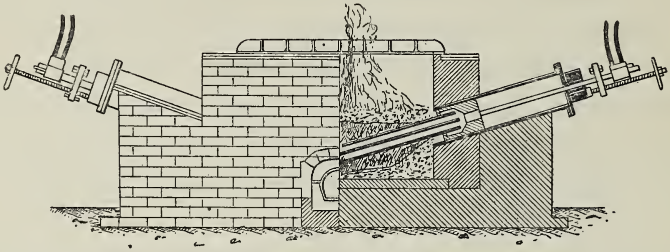


FIG. 5.—Cowles process. Apparatus employed at the Milton Works.

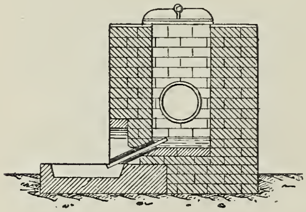


FIG. 6.—Cowles process. End view of the apparatus.

This process is employed by the "Cowles Syndicate," whose works are at Milton near Stoke-on-Trent; it is only suitable for the production of alloys.

II. *The Héroult process.*—This process, which is analogous to that of Cowles, is worked at Neuhausen near Schaffausen, and at Froges (Isère). The material employed is either bauxite, free from silica and iron, or else pure alumina.

The apparatus for treating this material consists of a crucible of pressed carbon clamped by iron plates (Fig. 7). It would appear that the first stage is the fusion of the alumina by the electric arc, the fused mineral then undergoing electrolysis. The bottom of the bath is formed by the metal to be alloyed, which acts as the negative pole. A description of the process is given by the inventor in a supplement (dated April 15, 1887) to his original patent of April 23, 1886, which relates to the electrolysis of alumina dissolved in molten cryolite.

III. *The Minet process.*—The bath is composed of 70 parts of sodium chloride and 30 parts of the double silicate of aluminium and sodium. For a current of 4000 ampères the weight of the charge amounts to about 176 lbs., and a temperature of about 800° is high enough to keep the bath in a sufficiently liquid state for the normal conduct of the electrolysis.

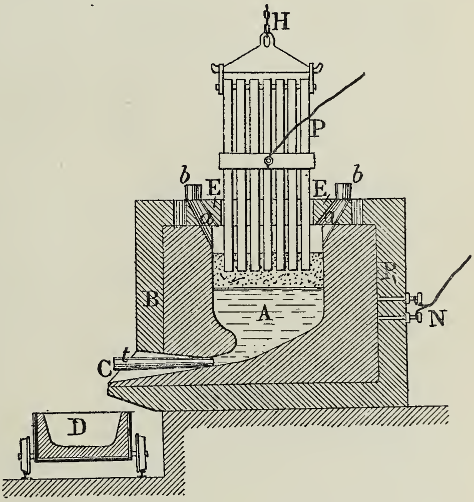


Fig. 7.—Héroult process.

The apparatus (Fig. 8) is composed of a parallelopiped metallic vat, the sides of which measure 12 to 20 inches in length according to the intensity of current employed. In order to enable the vat to resist the action of the molten fluoride, connection is established between the walls and the negative electrode by means of a resistance which allows only $\frac{1}{100}$ of the current to pass. By this means the sides are kept covered by a thin deposit of aluminium, which acts as a protective layer.

The electrodes are made of compressed carbon, and immediately below the cathode a small crucible is placed to collect the metal produced. When the current is passed the aluminium fluoride is decomposed, aluminium collecting at the negative pole, whilst at the same time an equivalent amount of fluorine is liberated at the positive pole. The bath is renewed, as decomposition proceeds, by a mixture of alumina and aluminium fluoride; and the alumina seizes upon a portion of the liberated fluorine to form aluminium fluoride, which thus regenerates the electrolyte.

The output of aluminium by this process is 25 grams per electrical horsepower hour, the cost of the motive power consumed in producing 1 lb. of the metal being about 2d.

3. **Properties of Aluminium.**—*A.* PHYSICAL PROPERTIES.—Aluminium is a dull white metal exhibiting a slight blue tinge in comparison with silver; it readily takes a fine polish. Its sp. gr. varies between 2·50 and 2·70, according to whether it has been cast or rolled. The specific heat is 0·2253; fusing point about 600° C.; and the metal is capable of retaining gases by occlusion.

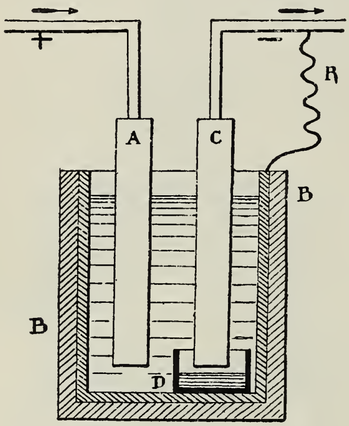


FIG. 8.—The Minet process.
B, vat; A, anode; C, cathode; R, resistance coil; D, collecting crucible.

When newly cast, aluminium is of equal hardness to virgin silver, but this quality is greatly increased by rolling, which treatment also imparts elasticity. In point of malleability the metal is comparable with gold and silver, and in tenacity it occupies a position between zinc and tin, or, when rolled, is equal in this respect to rolled copper.

Aluminium is easy to stamp, and can be forged without difficulty both cold and hot; it is, moreover, highly sonorous. Its atomic weight is 27, and it is regarded as a trivalent metal.

B. CHEMICAL PROPERTIES.—Aluminium must be looked upon as one of the most unalterable metals. It is unacted upon by air, whether moist or dry, and undergoes no change when fused in the open air, though when heated in a blast furnace it becomes covered with a thin layer of oxide. When it contains silicon the metal burns freely. It is readily soluble in hydrochloric acid or caustic alkalis, but offers considerable resistance to the action of nitric, sulphuric, and organic acids. Sulphur will not attack aluminium except at very high temperatures; and when extraneous metals, such as iron, copper, etc., are present, these latter become converted into sulphides at temperatures whereat aluminium does not undergo any change.

It combines readily with chlorine, bromine, and iodine under the influence of heat, and forms crystalline compounds with boron and silicon. Carbon, nitrogen, phosphorus, and arsenic have no effect upon it. With the majority of other metals aluminium forms interesting alloys.

Water is not decomposed by aluminium, even when the metal is heated nearly to the point of fusion.

Aluminium decomposes a very large number of metallic compounds in solution, by displacing and liberating the metal, the reaction being greatly facilitated by rendering the solution alkaline or ammoniacal.

Even in a molten state aluminium is unattacked by potassium nitrate, which, on this account, is used for refining the metal.

The physical and chemical properties are considerably modified by the presence of impurities, such as silicon, sodium, etc.

4. **Uses of Aluminium.**—Aluminium is employed for purifying other metals, most of the large steel works in France and Germany using pure aluminium for this purpose, whilst in England and the United States ferro-aluminium is utilised instead.

The resistance offered by this metal to oxidation, and its general properties, recommend it as a material for cooking utensils; numerous trials have been made, and are in progress, with reference to its use for military bottles, pannikins, harness fittings, etc.

Other applications for this metal are the manufacture of keys, optical, surgical, and physical appliances; its sonority renders it suitable for musical instruments and bells, and its lightness for the metallic fittings of balloons. Aluminium is also employed in the form of sheet metal in marine construction, and it is likewise used for making bicycles. The already extensive utility of this metal will be increased in proportion as improved methods of

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production enable it to be obtained in a pure state and at low cost, and its alloys are at present very largely employed.

§ 2. COMPOUNDS OF ALUMINIUM

5. **Aluminium Fluorides.**—*A.* ANHYDROUS ALUMINIUM FLUORIDE (Al_2F_6).—This compound may be prepared by treating calcined alumina with hydrofluoric acid in excess, the product being dried and distilled in a tubular carbon retort through which a current of hydrogen is passed (H. St. Claire Deville).

Another method is by fusing together a mixture of anhydrous aluminium sulphate and cryolite, the resulting sodium sulphate and insoluble aluminium fluoride being separated by lixiviation.

Grabau treats cryolite with a solution of aluminium sulphate, evaporating the mass to dryness and taking up the residue with water.

Brunner has shown that this salt may also be obtained by passing a current of gaseous hydrofluoric acid over alumina heated to redness in a platinum crucible.

Aluminium fluoride crystallises in rhombohedra (88° 30′), which are colourless, of low refraction, and frequently grouped into large agglomerations. These crystals are insoluble in acids, even in boiling sulphuric acid. Caustic potash solution scarcely affects them at all, and the only means of attack is by sodium carbonate at a red heat. When fused with boric acid they furnish crystallised aluminium borate.

B. HYDRATED ALUMINIUM FLUORIDE (Al_2F_6, $7H_2O$).—This is prepared by the action of dilute hydrofluosilicic acid on calcined alumina or kaolin. According to St. Claire Deville, a soluble aluminium silicate ($3SiF_4$, Al_2F_6) is first formed, but, on prolonging the digestion with alumina, silica is deposited and a neutral liquor containing the salt Al_2F_6, $7H_2O$ is left behind.

This hydrated fluoride is soluble, and is readily attacked by acids.

C. FLUO-ALUMINIC ACIDS.—Dilute hydrofluosilicic acid is allowed to react on calcined alumina, care being taken to preserve the liquid in a strongly acid state until the operation is completed.

Strong alcohol being then added, an oily precipitate is formed, which quickly solidifies and crystallises.

This product is a fluo-aluminic acid, having the formula $3Al_2F_6$, $4HF$, $10H_2O$.

If, instead of treating it with alcohol, the acid liquid is evaporated, hydrofluoric acid will be liberated, leaving a crystalline mass which, when washed with boiling water and dried, exhibits the composition Al_2F_6, HF, $5H_2O$.

The existence of these two fluo-aluminic acids, and the great difference between the anhydrous and the hydrated fluoride, led St. Claire Deville to consider cryolite (Al_2F_6, $6NaF$) as derived from an undiscovered fluo-aluminic acid, Al_2F_6, $6HF$, by the substitution of an equivalent quantity of sodium for the hydrogen. The hydrated aluminium fluoride would then be simply a fluo-aluminate of aluminium—

$$Al_2F_6,\ Al_2F_6 + 14H_2O = 2(Al_2F_6,\ 7H_2O),$$

the 6 atoms of hydrogen in Al_2F_6, $6HF$ being replaced by 2 atoms of aluminium. This would accord with what is known as to the trivalence of the metal.

The fluo-aluminic acids, free from silica, may be volatilised completely, yielding anhydrous aluminium fluoride, water, and hydrofluoric acid.

D. DOUBLE FLUORIDE OF ALUMINIUM AND SODIUM (CRYOLITE) (Al_2F_6, $6NaF$).—This double salt may be prepared by treating a mixture of alumina and sodium carbonate, in suitable proportions, with hydrofluoric acid, the liquid being evaporated and the excess of acid driven off from the residue by calcination.

Another method is to partially saturate a solution of hydrofluoric acid with alumina and then add sufficient sodium chloride to furnish 6 atoms of sodium per 2 atoms of aluminium, whereupon cryolite is precipitated.

This remarkable compound is met with in nature, the most important deposits being found on the coast of Greenland. Since 1855 it has been utilised in Denmark and Prussia, under the name of mineral soda, for soap-making, by treating the finely powdered mineral with boiling milk of lime, which precipitates calcium fluoride and leaves in solution an aluminate of sodium with an excess of caustic soda. Soaps made with this aluminate retain a very high percentage of water.

At the present time cryolite is used in the manufacture of aluminium, and as a flux.

6. **Aluminium Chlorides.** — *A.* ANHYDROUS ALUMINIUM CHLORIDE (Al_2Cl_6).—This chloride is prepared by intimately mixing 100 parts of calcined alumina with 40 parts of lampblack and enough oil to make a stiff paste, the whole being calcined in a covered crucible at a bright red heat. The resulting solid mass is broken in small pieces, which are placed in a tubulated retort fitted with a porcelain tube reaching to the bottom. The retort being set in a reverberatory furnace, the porcelain tube is connected with a chlorine generator; and in the neck of the retort is fitted the stem of a funnel, in the bowl of which is luted a gas jar provided with a delivery tube (Fig. 9).

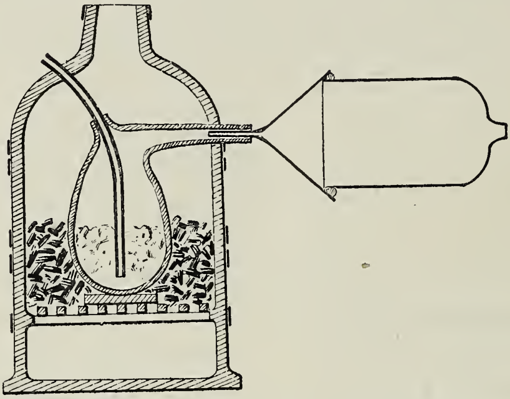


FIG. 9.—Preparation of aluminium chloride.

On heating the retort to redness and passing a current of chlorine, the aluminium chloride formed distils over and condenses in the gas jar in the form of a crystalline incrustation, which can be detached when the operation is completed.

For the preparation of this salt on an industrial scale St. Claire Deville replaced the above mixture by alumina and tar, and employed a gas retort set vertically in an enclosure traversed by the flame from a furnace, a brick-work condensing chamber being substituted for the gas jar.

Crude aluminium chloride is generally yellow in colour, owing to the presence of the sulphides of chlorine and iron. To purify the salt the above-named chemist proposed a method of sublimation over metallic iron, the ferric chloride being thereby reduced to non-volatile ferrous chloride, whilst the sulphur chloride is converted into sulphur and ferrous chloride.

Dumas proposed a second sublimation over finely divided aluminium.

The best results are obtained by the following process, devised by Weber:—

Aluminium chloride and powdered aluminium are introduced into a tube closed at one end and bent into the shape of a U. The other end being sealed in the lamp, heat is applied, the chloride fuses under the pressure of its own vapour and gradually becomes decolorised in contact with the metal; it can then easily be sublimed into the second branch of the tube. The chloride purified in this manner takes the form of a colourless transparent mass composed of hexagonal prisms. Under ordinary atmospheric pressure it readily sublimes without fusing. Nevertheless, when heated rapidly in large bulk it can be fused and even raised to ebullition. It fuses rapidly under pressure.

The actual fusing point is between 186° and 190°. Towards 400° C. the vapour density is very near 9·20, but diminishes to 4·6 at about 800°. The heat of combination is $Al_2Cl_6 = 321·96$ cal.; the heat of solution is $Al_2Cl_6Aq = 153·69$ cal.

Aluminium chloride is a highly deliquescent salt, which combines directly with phosphorus pentachloride to form a compound with the formula $2PCl_5, Al_2Cl_6$, a white mass capable of sublimation and fusing to a brown mass which boils at about 400°.

With phosphorus oxychloride it forms a double salt, $Al_2Cl_6, 2PO.Cl_3$, which, in an excess of the oxychloride, crystallises in colourless needles which fuse at 165° and volatilise without decomposition. It is broken up by the action of water.

Aluminium chloride absorbs sulphuretted hydrogen and furnishes small transparent crystalline lamellæ which are instantaneously destroyed by water, H_2S being disengaged.

When sublimed in a current of phosphuretted hydrogen, aluminium chloride yields a crystalline product, $3Al_2Cl_6 + 2PH_3$.

Aluminium chloride readily absorbs dry ammonia gas, sufficient heat being evolved to liquefy the compound, which corresponds to the formula $Al_2Cl_6, 6NH_3$. When distilled in hydrogen this product gives off ammonia and becomes converted into $Al_2Cl_6, 2NH_3$.

Sulphur dioxide combines slowly with aluminium chloride at the ordinary temperature, and more rapidly towards 50° C., furnishing a compound, $AlCl_2, SO_2Cl$.

In the laboratory, aluminium chloride is largely employed for synthetical experiments in organic chemistry (Friedel and Crafts' method).

B. HYDRATED ALUMINIUM CHLORIDE ($Al_2Cl_6, 12H_2O$).—This salt may be prepared from aluminium sulphate and barium chloride by double decomposition. The anhydrous chloride dissolves in water, with evolution of considerable heat, and the solution, on cooling, deposits crystals in the form of hexagonal prisms terminating in a rhombohedron (about 138°). The formula is $Al_2Cl_6, 12H_2O$. The same result is obtained by crystallisation in hydrochloric acid. Crystals of better shape are produced by heating aluminium hydroxide with concentrated hydrochloric acid in a sealed tube.

The following table gives the density of various solutions of aluminium chloride at 15° C.:—

Al_2Cl_6 per cent.	Sp. gr. at 15° C.	Al_2Cl_6 per cent.	Sp. gr. at 15° C.	Al_2Cl_6 per cent.	Sp. gr. at 15° C.	Al_2Cl_6 per cent.	Sp. gr. at 15° C.
2	1·0144	12	1·0890	22	1·1709	32	1·2615
4	1·0288	14	1·1047	24	1·1881	34	1·2808
6	1·0435	16	1·1207	26	1·2058	36	1·3007
8	1·0584	18	1·1379	28	1·2241	38	1·3211
10	1·0734	20	1·1537	30	1·2422	40	1·3415

The sp. gr. of the saturated solution (41·13 per cent.) is 1·3536. These solutions cannot be evaporated to complete dryness, because the hydrated chloride is then decomposed, water and hydrochloric acid being disengaged and aluminium deposited. When exposed *in vacuo* over concentrated sulphuric acid the crystallised hydrated chloride does not part with even a trace of its water of crystallisation.

C. DOUBLE CHLORIDES OF ALUMINIUM.—Aluminium chloride combines with alkali chlorides to form veritable chlorinated spinelles, having the general formula $2R.Cl, Al_2Cl_6$. These products fuse at about 200° C., and are volatile at red heat; when dissolved in water they furnish a mixture of the two salts, crystallising separately.

The most important of these double chlorides is that of aluminium and sodium, which is prepared by passing a current of chlorine through a mixture of alumina and carbon with an addition of common salt.

It is a colourless, crystalline substance, fusing at about 185° and volatilising at red heat, and is very hygroscopic, though less so than aluminium chloride.

D. BASIC CHLORIDES.—Liechti and Suida have prepared solutions corresponding to the following salts:—

$$Al_2Cl_6,$$
$$Al_2Cl_5(OH),$$
$$Al_2Cl_4(OH)_2,$$
$$Al_2Cl_3(OH)_3,$$
$$Al_2Cl_2(OH)_4,$$

though they did not succeed in isolating any of them. The solutions are decomposed by heat or by dilution with water.

7. **Aluminium Bromide** (Al_2Br_6) may be prepared by slowly pouring bromine over finely divided aluminium, sufficient heat being evolved during combination to raise the aluminium to incandescence.

The best method of preparation, however, is by passing bromine vapour over aluminium in a glass tube heated to incipient redness. The product, which may be purified by passing its vapour over aluminium, is colourless, and crystallises in the form of small brilliant flakes. It fuses at 93° to a limpid mobile liquid boiling at 260°; the density in the solid state is 2·54; vapour density, 18·62 (Deville and Troost); heat of formation, $Al_2Br_6 = 239{\cdot}44$ cal.; heat of solution, $Al_2.Br_6 = 170{\cdot}60$ cal. It is very hygroscopic.

8. **Aluminium Iodide** (Al_2I_6).—Given a sufficiently high temperature, iodine and aluminium combine directly, with evolution of sufficient heat to raise the mass to incandescence. The usual method of preparation is by passing iodine vapour over red-hot aluminium, the product being purified in the same manner as for the bromide.

The resulting compound is a colourless solid, crystallisable by fusion. It melts at 125° and boils at 350°, but can only be distilled in an atmosphere of inert gas, since above this temperature it explodes when mixed with air, and furnishes alumina and iodine. The double iodide Al_2I_6, 2KI fuses readily, and may be heated much above the fusing point of aluminium iodide without undergoing any change.

According to Berthelot, the heat of formation of this compound is $Al_2I_6 = 140{\cdot}78$ cal., and the heat of solution, Al_2I_6, Aq. $= 178$ cal. The density in the solid state is 2·63, and the vapour density at 440° is 27, the theoretical density for $Al_2I_6 =$ 2 vols., being 28·3. The difference between these last two values is attributed by Deville and Troost to the instability of this iodide, which becomes partially decomposed at the temperature of the experiment.

Aluminium iodide is soluble, at the ordinary temperature, in 3 times its own weight of carbon disulphide; it is also soluble in alcohol and ether, is deliquescent, and dissolves in water with evolution of heat.

9. **Alumina.**—*A.* ALUMINIUM SESQUIOXIDE, or ALUMINA (Al_2O_3), is obtained on dehydrating the hydroxide by heat, or by subjecting ammonium alum to strong calcination.

Pure alumina is a light, white powder, devoid of odour or flavour; hygrometric, adherent to the tongue, and very refractory. In the oxyhydrogen furnace it yields a very fluid globule, which on cooling re-crystallises to an extremely hard mass capable of cutting glass. The heat of formation from its elements is $Al_2O_3 = 196{\cdot}3$ cal.

Calcined alumina is totally insoluble in water, but if not heated above dark redness it is capable of re-hydration, heat being evolved. When calcined and re-cooled in a moist atmosphere it will absorb and tenaciously retain up to 15 per cent. of its own weight of water.

Its solubility in acids varies with the method of preparation employed. If calcined very strongly it becomes very slightly soluble, even in hot concentrated acids. Alkaline solutions also dissolve it with great difficulty, but it may be easily converted into a soluble aluminate by calcination with caustic potash or soda (or even with an alkali carbonate) in a silver crucible.

B. ALUMINIUM HYDROXIDE (Al_2O_3, $3H_2O$).—I. *Ordinary Hydrate.*—The heat of formation from its elements $Al_2.O_3$, $3H_2O$ = 197·8 cal.

The voluminous, gelatinous precipitate obtained on treating a soluble salt of aluminium by ammonia is readily soluble in dilute acids and alkalis, and when dried at 100° C. exhibits the composition Al_2O_3, $3H_2O$.

A much denser form of the same hydrate can be prepared, as a granular precipitate free from iron, by passing a current of carbon dioxide through a cold dilute solution of sodium aluminate. The hydrate thus obtained is insoluble in acetic acid.

If the precipitate formed by ammonia be boiled for some time in water it undergoes dehydration and is converted into Al_2O_3, $2H_2O$, which, like calcined alumina, is insoluble in weak acids and dilute alkalis.

Aluminium hydrate possesses great affinity for organic substances, a property which accounts for its extensive use in dyeing.

II. *Soluble Alumina.*—Successful attempts have been made to obtain alumina in the soluble form. Walter Crum prepared it by heating a dilute solution of aluminium bi-acetate in a closed vessel, for ten days and nights, in boiling water.

On then boiling the solution for an hour or two, and replacing the water lost by evaporation, all the acetic acid is driven off and there remains a transparent, insipid solution of soluble alumina, which becomes gummy when concentrated, and coagulates to a firm jelly on the addition of a small quantity of alkali or acid. When evaporated on the water bath it yields the hydroxide Al_2O_3, $2H_2O$.

Soluble alumina was also obtained by Graham by dialysing aluminium chloride containing an excess of alumina in solution; but whereas the "metalumina" prepared by Crum does not act as a mordant, the product obtained by Graham possesses mordanting properties.

For the rest, both varieties are coagulated to a firm jelly by small quantities of acids, alkalis, or various salts, a property utilised in bacteriology for the preparation of certain special culture media.

C. OCCURRENCE IN NATURE. PREPARATION OF CRYSTALLINE ALUMINA.—Alumina in a pure state is somewhat rare in nature. In the condition of colourless crystals it forms corundum; and when crystalline and coloured by various oxides it is known under the names of ruby, oriental topaz, oriental sapphire, amethyst, etc.; whilst, in admixture with ferric oxide, alumina constitutes emery.

Several natural hydroxides are known. Gibbsite, Al_2O_3, $3H_2O$, corresponds to the ordinary hydrate; diaspore exhibits the formula Al_2O_3, H_2O. Bauxite, another natural hydroxide of variable composition, but approximating most nearly to Al_2O_3, $2H_2O$, is particularly abundant. Important deposits are met with in France, particularly near Tarascon.

Corundum was first artificially prepared by Ebelmen, by heating a mixture of alumina and sodium borate in a porcelain furnace, the alumina crystallising in proportion as the sodium borate is volatilised. By the addition of a little chromic oxide to the mixture, ruby is obtained.

Corundum was also prepared by St. Claire Deville and Caron, by heating, in a carbon crucible, a fluoride above which is placed a small platinum crucible containing boric acid. At a high temperature the fluoride reacts on the boric acid, forming boron fluoride and a crystallised oxide, which may be coloured by the addition of some pigmentary oxide.

De Senarmont has obtained a mixture of corundum and diaspore by strongly heating a dilute solution of aluminium chloride.

10. **Aluminates.**—Alumina will combine with alkalis, baryta, etc., to form soluble products, whilst lime yields an insoluble product. These bodies constitute the aluminates.

A fairly large number of natural aluminates are known, viz., the spinelle ruby (magnesium aluminate); gahnite (zinc aluminate); hercytine (iron aluminate), crystallising in octahedra; cymophane (glucinum aluminate), crystallising according to the right rhomboidal prism system.

The general formula for these aluminates is

$$RO.Al_2O_3.$$

Ebelmen reproduced them by heating, in presence of boric acid, a mixture of alumina with the oxide forming the base of the desired aluminate. To obtain balas ruby it is sufficient to add to the mixture a trace of potassium dichromate.

Cymophane and gahnite have been reproduced by Deville and Caron, by heating a mixture of the fluorides of aluminium and glucinum, or zinc, in a carbon crucible containing a small platinum capsule filled with boric acid.

Stanislas Meunier prepared artificial spinelle by strongly heating, for several hours, a mixture of cryolite and aluminium chloride covered with alumina and magnesia in a carbon crucible brasqued with magnesia.

A. POTASSIUM ALUMINATE ($K_2Al_2O_4$, $3H_2O$).—This aluminate may be regarded as derived from the hydroxide

$$Al_2O_3, H_2O = \left.\begin{matrix}Al_2\\H_2\end{matrix}\right\}\overset{\text{VI}}{O}_4.$$

It is prepared either by dissolving gelatinous alumina in caustic potash, or by heating a mixture of alumina with an excess of potash, to the point of fusion in a silver crucible. On evaporating the solution *in vacuo* hard and brilliant crystals of potassium aluminate are obtained, and may be purified by re-crystallisation. It is a white substance, very soluble in water but insoluble in alcohol, with a caustic taste and alkaline reaction. In presence of a large volume of water it undergoes decomposition, alumina being precipitated.

B. SODIUM ALUMINATE ($Na_6Al_4O_9$) may be considered as derived from the hydroxide

$$2Al_2O_3 + 3H_2O = \left.\begin{matrix}2Al_2\\H_6\end{matrix}\right\}O_9.$$

It is prepared in the same way as the potassium salt, by substituting caustic soda for potash, and is very soluble in water, the solution gradually becoming covered with a layer of sodium carbonate when evaporated in an open vessel.

Apart from its use in dyeing, this product is of great industrial interest for the preparation of iron-free alumina, which is utilised for the manufacture of aluminium and for the production of pure aluminium sulphate and alum.

On a manufacturing scale it is prepared by heating to redness a mixture of 1 part of Na_2CO_3 and 2 parts of bauxite free from silica, the fritted mass being extracted with water. From this solution the alumina is separated either by the action of carbon dioxide or by agitation, a small quantity of recently precipitated alumina being added to facilitate precipitation (Baeyer process).

According to Cavazzi, the compound $Al_2O_2(NaO)_2$ is obtained when aluminium is dissolved in caustic alkali.

C. BARIUM ALUMINATE ($Al_2O_4Ba, 4H_2O$).—This salt was prepared by Deville, by heating to redness a mixture of alumina and caustic baryta (barium hydroxide). It is soluble in water, from which it is thrown down as a crystalline precipitate by alcohol.

Other aluminates of barium, having the formulæ
$Al_2O_3, 3BaO, 5H_2O$; $Al_2O_3, BaO, 7H_2O$; $Al_2O_3, 3BaO, nH_2O$
have been obtained from baryta water and alumina.

D. CALCIUM ALUMINATE.—Ebelmen prepared a crystalline calcium aluminate of the formula Al_2O_4Ca. The compounds of alumina and calcium are insoluble, and some of them appear to play a part in the hardening of cement.

Many other aluminates are known, but the only compound of this class really possessing any industrial interest is sodium aluminate.

11. **Aluminium Sulphide.**—Aluminium is not attacked by sulphur except at a very high temperature. On bringing sulphur into contact with the red-hot metal, combination occurs and is accompanied by evolution of heat.

Aluminium sulphide may be prepared by passing sulphur vapour, in a current of hydrogen, over aluminium heated to redness; and Fremy has obtained it by passing the vapour of carbon disulphide over white-hot alumina in a platinum capsule, carbon oxysulphide being formed at the same time.

Aluminium sulphide is a pale yellow substance, fusible with difficulty, and setting to a crystalline mass on cooling. In moist air it decomposes, sulphuretted hydrogen being given off; and water decomposes it instantly, with evolution of sulphuretted hydrogen and deposition of alumina. When heated to redness and exposed to steam it is also broken up, an extremely hard residue of crystalline alumina being left.

12. **Aluminium Sulphite.**—Alumina precipitated from its salts easily dissolves in sulphurous acid, whereas the alumina of aluminates is insoluble therein.

Aluminium sulphite is very soluble in water, the solution yielding a gummy mass on evaporation *in vacuo.* Heated gently, it gives off sulphur dioxide, and, according to Gougginsperg, if the heating be continued until the evolution of gas ceases, a precipitate of $SO_3(Al_2O_2)''$, $4H_2O$ is formed.

Another method of preparation is by heating a concentrated solution of sodium sulphide with aluminium sulphate; on cooling, sodium sulphate crystallises out, leaving aluminium sulphite in solution.

Jacquemart prepared it by passing a current of sulphur dioxide through a solution of sodium aluminate, the effect of which is to throw down a basic aluminium sulphite, sodium bisulphite remaining dissolved. The precipitate is collected and dissolved in an excess of sulphurous acid.

Aluminium sulphite has been utilised in the sugar industry, for purifying the syrup.

13. **Aluminium Sulphates.**—*A.* NORMAL ANHYDROUS SULPHATE $(SO_4)_3Al_2$.—This salt is prepared by dehydrating the crystallised sulphate by heat. It is a white substance of sp. gr., 2·710 (Nilson and Petterson); the specific heat is 0·1855; molecular heat, 63·59; and molecular volume, 126·50. When heated to redness it parts with its sulphuric acid, anhydrous alumina, Al_2O_3, being left behind, prolonged exposure to strong heat being, however, required to drive off the final traces of the acid, which are somewhat tenaciously retained. All the basic

salts of aluminium obtained by precipitating the sulphate by ammonia, calcium carbonate, etc., behave in the same way.

Hydrogen reduces anhydrous aluminium sulphate at red heat, water and sulphur dioxide being liberated, and alumina—almost entirely free from sulphuric acid—left. Ammonium chloride also decomposes this sulphate, with the assistance of heat, and gives rise to volatile products.

When fused with sulphur the anhydrous sulphate is reduced to sulphide, with evolution of sulphur dioxide. When treated several times in succession with hydrochloric acid, in the warm, a small portion is converted into aluminium chloride.

The solubility of aluminium sulphate varies according to the temperature, Poggiale giving the following values per 100 parts of water:—

Temperature.	$(SO_4)_3Al_2$ dissolved.	Temperature.	$(SO_4)_3Al_2$ dissolved.
0°	31·30	60°	59·09
10°	33·50	70°	66·23
20°	36·15	80°	73·14
30°	40·36	90°	80·83
40°	45·73	100°	89·11
50°	52·13		

B. ORDINARY ALUMINIUM SULPHATE, $(SO_4)_3Al_2$, $18H_2O$, is a white salt, occurring most frequently in masses resembling fat in consistency; also as powder, lumps, etc. It is greasy and unctuous to the touch, and is deliquescent when an excess of sulphuric acid is present. It is extremely soluble in water, and crystallises, though with difficulty, in needles or nacreous white scales. Handsome crystals may be obtained by leaving a concentrated solution of aluminium sulphate for a considerable time in absolute quietude in a large uncovered beaker. The crystalline habit is that of an orthorhombic prism, considerably flattened along g^1, with the faces mh^1a^1 scarcely developed at all. When perfectly free from sulphuric acid the salt is efflorescent.

The flavour is sweet at first, but astringent afterwards.

Aluminium sulphate is generally regarded as a hydrate (sp. gr., 1·767 at 22°) containing 18 molecules of water, but, according to P. Margueritte Delacharlonny, the proper formula for the typical hydrate should be $(SO_4)_3Al_2$, $16H_2O$.

In solution, aluminium sulphate is acid to litmus paper, and turns Congo-red blue. It is almost insoluble in alcohol, but dissolves readily in hot hydrochloric acid, handsome colourless tablets being obtained as the solution cools down. Under the influence of heat it swells up and loses water, a porous mass of low solubility being left. When heated to redness it leaves an alumina tenaciously retentive of the final traces of sulphuric acid.

On treating an aqueous solution of aluminium sulphate with alcohol a precipitate of hard nacreous flakes consisting of $(SO_4)_3Al_2, 10H_2O$ is obtained, which when gradually heated parts with water and sulphuric acid, leaving behind a skeleton of insoluble alumina retaining the form of the original crystals. On the other hand, in contact with moist air, the precipitate absorbs water and is converted into $(SO_4)_3Al_2, 18H_2O$.

Aluminium sulphate in solution is decomposed by calcium carbonate, zinc, etc., forming with the first-named reagent calcium sulphate, an insoluble basic aluminium sulphate, and carbon dioxide, the latter being disengaged. Zinc gives in the warm an abundant liberation of hydrogen, zinc sulphate, and a subsulphate of aluminium, $3(SO_4Al_2O_2), 2Al_2O_3 + 20H_2O$, being formed. In the cold the reaction is less rapid, but the mass gelatinises by degrees, and here again a sub-salt is produced, represented by the formula $3(SO_4.Al_2O_2)Al_2O_3, 36H_2O$. The same product in a different form is also obtained from the reaction of calcium carbonate on alum (H. Debray). These basic salts will be more fully discussed later on.

On heating a concentrated solution of sodium sulphite with aluminium sulphate and leaving to cool, crystals of sodium sulphate are obtained, whilst aluminium sulphite remains in solution (Manzoni).

A concentrated solution of aluminium sulphate forms an excellent reagent for salts of potassium, ammonium, etc., by producing a highly characteristic precipitate of alum.

Aluminium sulphate is found in nature. The commercial product assumes the form of cakes, blocks, lumps, powder, etc., and is more or less dry according to the degree of concentration before casting. It is opaque and white, the whiteness being more pronounced as the salt is purer. Ferrous sulphate imparts a greenish tinge, whilst in presence of ferric sulphate a reddish coloration appears; and aluminium sub-sulphate turns the mass yellow. When cast in cakes, aluminium sulphate resembles fat or alabaster in appearance, and after a time the cakes assume a crystalline texture in the case of the pure salt. The commercial sulphate often contains free sulphuric acid and potash alum.

Aluminium sulphate is extremely soluble in water, the figures given by Poggiale per 100 parts of water being

Temperature.	$(SO_4)_3Al_2$, $18H_2O$ dissolved.	Temperature.	$(SO_4)_3Al_2$, $18H_2O$ dissolved.
0°	86·85	60°	262·20
10°	95·80	70°	348·20
20°	106·35	80°	467·30
30°	127·60	90°	678·80
40°	167·60	100°	1132·00
50°	201·40		

We are indebted to Reuss for the determination of the density of solutions of pure aluminium sulphate, and of the commercial sulphate prepared from alunite; the latter invariably contains potash alum.

The following table gives the density and corresponding percentage of $(SO_4)_3Al_2$ of these solutions at different temperatures:—

$(SO_4)_3Al^2$ per cent.	Pure Salt.	Commercial Salt.	$(SO_4)_3Al_2$ per cent.	Pure Salt.	Commercial Salt.	$(SO_4)_3Al_2$ per cent.	Pure Salt.	Commercial Salt.
	t=15° C.		17	1·1770	1·1199		t=35° C.	
1	1·017	1·0069	18	1·1876	1·1269	5	1·045	1·0270
2	1·027	1·0141	19	1·1971	1·1339	10	1·096	1·0627
3	1·037	1·0221	20	1·2074	1·1440	15	1·146	1·0974
4	1·047	1·0299	21	1·2168	1·1448	20	1·192	1·1313
5	1·0569	1·0377	22	1·2274	1·1589	25	1·2407	1·1660
6	1·0670	1·0416	23	1·2375	1·1628			
7	1·0768	1·0481	24	1·2473	1·1689			
8	1·0870	1·0592	25	1·2572	1·1798			
9	1·0968	1·0650						
10	1·1071	1·0730					t=45° C.	
11	1·1171	1·0794		t=25° C.		5	1·0356	1·0179
12	1·1270	1·0860	5	1·0503	1·033	10	1·0850	1·0534
13	1·1369	1·0960	10	1·1022	1·0689	15	1·1346	1·0871
14	1·1467	1·1059	15	1·1522	1·1034	20	1·1801	1·1215
15	1·1574	1·1097	20	1·2004	1·1381	30	1·2295	1·1563
16	1·1668	1·1169	25	1·2483	1·1743			

C. Basic Aluminium Sulphates.—Of these a large number are known, and, while many of them are probably mixtures, they are for the most part of little importance, though some possess a certain decided interest in view of their utility in dyeing.

Some of these basic sulphates are soluble in water. If solutions of the normal sulphate are partly neutralised by carbonates of the alkalis or alkaline earths, by aluminium hydroxide, etc., solutions of basic sulphates are obtained, the salts varying in composition according to the degree of neutralisation.

With sodium bicarbonate, for example, the following sulphates may be produced:—

$$(SO_4)_3Al_2,\ 18H_2O + 2CO_3NaH$$
$$= (SO_4)_2Al_2O,\ H_2O + SO_4Na_2 + 2CO_2 + 18H_2O.$$

$$2[(SO_4)_3Al_2,\ 18H_2O] + 6CO_3NaH$$
$$= (SO_4)_3Al_2,\ Al_2O_3,\ 3H_2O + 3SO_4Na_2 + 6CO_3 + 36H_2O.$$

$$(SO_4)_3Al_2,\ 18H_2O + 4CO_3NaH$$
$$= SO_4Al_2O_2,\ 2H_2O + 2SO_4Na_2 + 4CO_2 + 18H_2O.$$

The basic aluminium sulphates may be regarded as derived from sulphuric acid (H_2SO_4) by the substitution of the oxygenated radicles Al_2O and Al_2O_2 for hydrogen, or they may be considered as the result of a union of two sulphates of the following types:—

$3H_2SO_4$ . . .	$(SO_4)_3Al_2^{(vi)}$,
$2H_2SO_4$ . . .	$(SO_4)_2(Al_2O)^{(iv)}$,
H_2SO_4 . . .	$SO_4(Al_2O_2)''$.

Again, they may be also regarded as resulting from the displacement of one or two divalent groups SO_4 in the normal sulphate $(SO_4)_3Al_2$, by 1 or 2 divalent atoms of oxygen.

According to Berzelius, a basic sulphate is produced when an aqueous solution of normal aluminium sulphate is precipitated by an insufficiency of ammonia. The formula of the washed and dried precipitate is given as

$$SO_4(Al_2O_2)'',\ 9H_2O = (SO_4,\ O_2)Al_2,\ 9H_2O.$$

This compound is met with in nature in the form of a white earthy mass (Websterite) of sp. gr. 1·705.

According to Bley, when a solution of alum or aluminium sulphate is treated with a quantity of ammonia insufficient to throw down the whole of the alumina, and the precipitate is left to collect for two or three days, a sub-salt corresponding to the formula

$$(SO_4)_2Al_2O, 2Al_2O_3, 20H_2O$$

is obtained after filtering and washing.

Alum, precipitated by ammonium carbonate under the same conditions, gives the same sub-salt, which, however, always retains 1 per cent. of potash.

When, according to the same author, a solution of alum is treated with potassium hydroxide or carbonate, avoiding an excess of the reagent, the precipitate, which only collects very slowly, has the formula

$$SO_4Al_2O_2, Al_2O_3, 12H_2O.$$

If a solution of aluminium acetate, containing not more than 0·3 per cent. of alumina, is treated with potassium sulphate and kept at a temperature of 38°, there results, according to Walter Crum, a precipitate of basic sulphate, which settles down gradually and contains all the alumina in the solution, its formula being

$$SO_4Al_2O_2, Al_2O_3, 10H_2O.$$

Certain natural products, such as *felsobanite*, $SO_4Al_2O_2$, Al_2O_3, $10H_2O$, and *paraluminite*, $SO_4Al_2O_2$, Al_2O_3, $15H_2O$, exhibit analogous composition.

A basic sulphate is easily obtained by heating a concentrated aqueous solution of aluminium sulphate with aluminium hydroxide. The resulting salt has, according to Maus, the following composition:—

$$(SO_4)_2Al_2O, nH_2O.$$

It is encountered in nature, in the anhydrous condition, as alumiane.

According to Marguerite, when alumina in any desired quantity is dissolved in the neutral sulphate, or the latter is treated with zinc, or potash- or ammonium alum is heated with care, an identical product, $(SO_4)_2Al_2O$, $12H_2O$, is always obtained.

When a concentrated solution of aluminium sulphate is boiled with aluminium hydroxide a gummy mass is obtained, which contains twice as much alumina, in proportion to the amount of acid, as is present in the neutral sulphate. This product is soluble in a small volume of water, but, if boiled in a larger quantity of that liquid, breaks up into normal sulphate, which remains in solution, and a precipitate of more highly basic sulphate, believed by Berzelius to have the composition

$$2(SO_4Al_2O_2) + (SO_4)_2Al_2O + 30H_2O.$$

On saturating very dilute sulphuric acid with aluminium hydroxide and setting it aside for some years, Rammelsberg obtained a crop of transparent, microscopic needles of the above composition.

In contact with a hot solution of neutral aluminium sulphate, zinc liberates an abundant volume of hydrogen. By heating a similar solution with zinc in a platinum capsule Debray obtained an easily washed granular precipitate, soluble in dilute acids, and having the formula

$$3(SO_4, Al_2O_2), 2Al_2O_3, 20H_2O.$$

In the cold the reaction is slower. On leaving a cold solution of aluminium sulphate in contact with zinc and platinum for eight days the same experimenter obtained a gelatinous precipitate, which, when washed and dried, consisted of hard lumps with a vitreous fracture, and exhibiting the composition

$$3(SO_4Al_2O_2), Al_2O_3, 36H_2O.$$

Debray also obtained the same salt, as a crystalline precipitate, by digesting calcium carbonate with a cold solution of ordinary alum.

When zinc and platinum are simultaneously introduced in a cold aqueous solution of alum, the zinc gradually dissolves, with evolution of hydrogen, and a crystalline precipitate of $5(SO_4Al_2O_2), 3Al_2O_3, 25H_2O$ is formed. Athanesco obtained a basic sulphate, with the formula $2(SO_4Al_2O_2), (SO_4)_2Al_2O, 9H_2O$, by heating a 3 per cent. solution of neutral aluminium sulphate to about 250°. This salt crystallised in small, colourless, transparent rhombohedra, greatly resembling cubes.

An aqueous solution of neutral aluminium sulphate, containing sodium chloride, heated to 130° – 140° for 2 hours, furnished Böttinger with a white, pulverulent precipitate, insoluble in water and acetic acid. At red heat it parted with only 2 molecules of water, and its composition corresponded to $SO_4Al_2O_2, 6H_2O$.

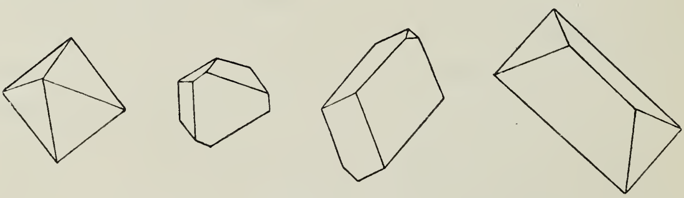
The existence of basic sulphates as so many separate chemical entities has been denied by certain authors. S. U. Pickering states that he failed to obtain basic sulphates of constant composition.

14. **Alums.**—*A.* General Remarks.—Aluminium easily forms double salts with metals, the alums being the most important compounds of this class.

The name alum is given to a remarkable series of bodies, typified by potash alum, to which alone the generic term was formerly applied.

The general formula is $(SO_4)_3M_2, SO_4R_2, 24H_2O$.

All the alums are more or less soluble in water and crystallise in regular octahedra, though at first sight the octahedron is not always recognisable in the crystals obtained, since the volume and the relative dimensions of the facets and edges may vary considerably according to the conditions under which crystallisation was effected. Nevertheless, though these conditions may produce deformations totally modifying the external appearance, the dihedral angles formed by the intersection of the facets always remain unchanged. The various shapes assumed by the octahedron are shown in Figs. 10 to 13.



Figs. 10 to 13.

The alums differ from one another only because the alumina and potash may be replaced, wholly or in part, by isomorphous substances. For example, alumina may be replaced by the sesquioxides of iron, manganese, chromium, etc., whilst the place of potash may be filled by soda, ammonia, the oxides of rubidium, cesium, thallium, etc.

Alums with organic bases have also been prepared, such as

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trimethylamine alum, ethylamine alum, methylamine alum, and amylamine alum; and selenic acid, which is isomorphous with sulphuric acid, may replace the latter in combination, and thus also furnish alums.

Furthermore, mixed alums may be prepared by mixing solutions of different alums together and leaving them to crystallise, the formation of crystals being facilitated in some cases by adding a certain quantity of ordinary alum to the solution. Thus iron alums with a base of thallium are more easily obtained as large crystals when part of the ferric oxide is replaced by an equivalent quantity of alumina.

A crystal of any alum may be developed in a solution of some other alum, by reason of the isomorphism of these salts; and it is for this reason that a crystal of chrome alum may be grown in a solution of ordinary alum, and *vice versâ.*

The method of naming these compounds makes them easily recognisable. If merely the name of the metal or oxide replacing potash is given, the alum always contains alumina.

For example:

Sodium alum = $(SO_4)_3Al_2, SO_4Na_2 + 24H_2O$.

Ammonium alum = $(SO_4)_3Al_2, SO_4(NH_4)_2 + 24H_2O$.

When only the name of the metal or oxide taking the place of the alumina is given, potassium is always the second metal.

For instance: chrome alum = $(SO_4)_3Cr_2, SO_4K_2 + 24H_2O$.

If the place of the two metals aluminium and potassium is occupied by isomorphous bodies, the names of both substitutes are given in speaking of the resulting alum.

Thus: ferro-ammonium alum = $(SO_4)_3Fe_2, SO_4(NH_4)_2 + 24H_2O$.

When the acid is other than sulphuric acid it also is specified.

At present a number of alums are known, among which the following may be cited:—

Ordinary alum	$(SO_4)_3Al_2, SO_4K_2 + 24H_2O$.
Ammonium alum	$(SO_4)_3Al_2, SO_4(NH_4)_2 + 24H_2O$.
Sodium alum	$(SO_4)_3Al_2, SO_4Na_2 + 24H_2O$.
Rubidium alum	$(SO_4)_3Al_2, SO_4Ru_2 + 24H_2O$.
Cesium alum	$(SO_4)_3Al_2, SO_4Ce_2 + 24H_2O$.
Thallium alum	$(SO_4)_3Al_2, SO_4Tl_2 + 24H_2O$.

Manganese alum	$(SO_4)_3Mn_2, SO_4K_2 + 24H_2O$.
Chrome alum	$(SO_4)_3Cr_2, SO_4K_2 + 24H_2O$.
Iron alum	$(SO_4)_3Fe_2, SO_4K_2 + 24H_2O$.
Chrome-ammonium alum	$(SO_4)_3Cr_2, SO_4(NH_4)_2 + 24H_2O$.
Ferro-ammonium alum	$(SO_4)_3Fe_2, SO_4(NH_4)_2 + 24H_2O$.
Ferro-thallium alum	$(SO_4)_3Fe_2, SO_4Tl_2 + 24H_2O$.
Selenium alum	$(SeO_4)_3Al_2, SeO_4K_2 + 24H_2O$.

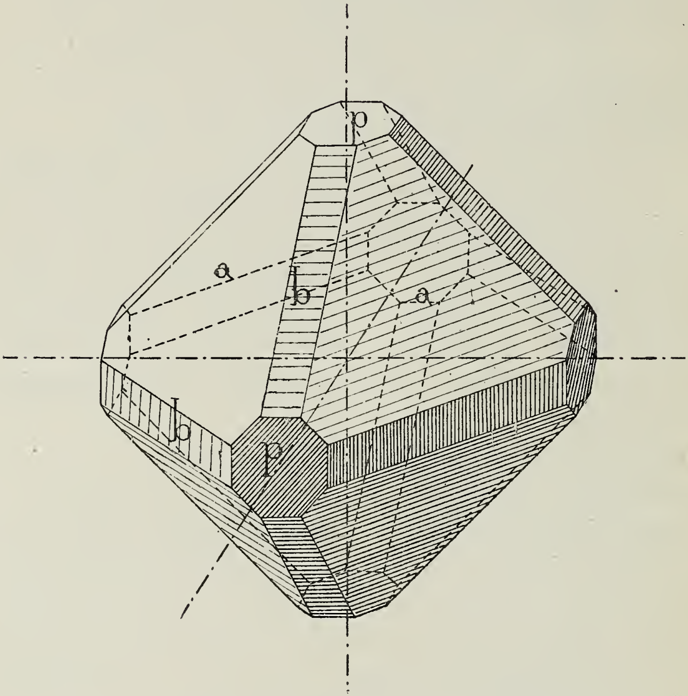


Fig. 14.—Octahedron modified by facets of the cube and the rhomboidal dodecahedron.

The organic alums having been already mentioned, need not be referred to again.

In the same manner that basic sulphates are prepared from aluminium sulphate, alums may be made to yield double basic salts, which are, moreover, found in nature, *e.g.*, alunite, lœvigite.

Whilst some of these compounds are merely of theoretical interest, others have found extensive application, and form the object of considerable industrial and commercial enterprise. A description of the principal kinds will now be given.

B. POTASSIUM (POTASH) ALUM.—I. *Ordinary Alum* $(SO_4)_3Al_2$, $SO_4K_2 + 24H_2O$. — In the laboratory this salt is prepared by dissolving and crystallising together equivalent proportions of pure aluminium sulphate and potassium sulphate. It may be purified by successive re-crystallisations, provided no other alum, even in small amount, is present; otherwise separation is very difficult, if not quite impossible.

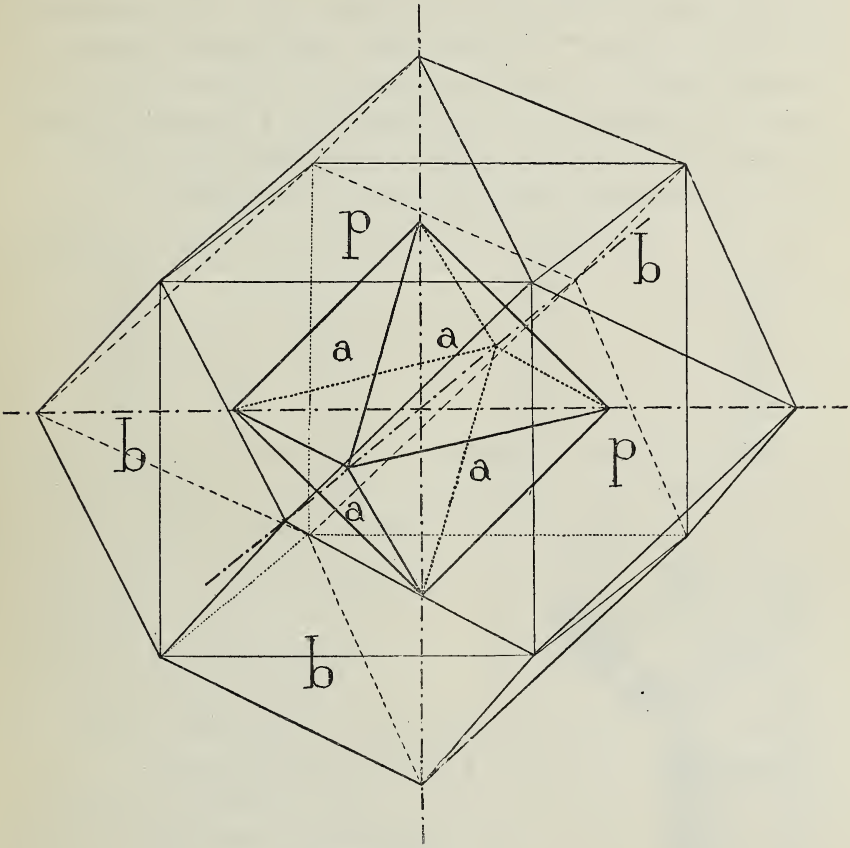


FIG. 15.

When dissolved, alum exhibits an acid reaction and a sweet flavour with an astringent after-taste. It crystallises in regular octahedra, which may be obtained of large size, colourless, and transparent. The most frequent modification of the crystals is by facets of the cube and the rhomboidal dodecahedron (Fig. 14), and such modifications are easily produced.

Fig. 15 shows the relation between the crystal and the cube, and dodecahedron.

The solution of ordinary alum can be supersaturated with ease; and alcohol will precipitate the salt from its solutions.

When freshly prepared the crystals are translucent, but become opaque after a lapse of some days. On exposure to the air for some considerable time they become milky and resemble marble or alabaster, by reason of a slight efflorescence, and more particularly by the formation of a superficial layer of a sub-salt under the influence of atmospheric ammonia.

According to Poggiale, 100 parts of water dissolve

Temperature.	$(SO_4)_3Al_2, SO_4K_2+24H_2O$ dissolved.	Temperature.	$(SO_4)_3Al_2, SO_4K_2+24H_2O$ dissolved.
0°	3·90	60°	66·65
10°	9·52	70°	90·67
20°	15·13	80°	134·47
30°	22·10	90°	209·31
40°	30·92	100°	357·48
50°	44·11		

When kept over sulphuric acid in a closed vessel, or heated to 61°, alum loses 18 molecules of water (Graham); and at 92·5° it melts in its own water of crystallisation. If the temperature be increased, dehydration gradually ensues, and the whole 24 molecules of water (45·5 per cent. of the total weight) are parted with by degrees.

When heated to redness in a crucible, alum swells up and projects far above the mouth of the vessel (Fig. 16). The porous and friable mass thus obtained forms the calcined alum employed as a caustic. At a bright red heat alum is decomposed, sulphur trioxide being given off together with sulphur dioxide and oxygen, whilst alumina and potassium sulphate are left behind. If the temperature be raised still higher, and the heating prolonged, potassium aluminate will be formed.

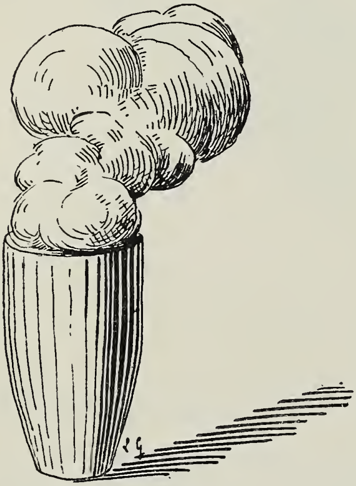


Fig. 16.

On exposing a mixture of 3 parts of calcined alum and 1 part of lampblack to moderate heat, in a crucible, a pulverulent mass, igniting spontaneously in contact with air (Homberg's pyrophore), is obtained. This consists of a very finely divided mixture of alumina, carbon, and potassium sulphide.

Crystallised anhydrous alum may be prepared by heating to fusion a mixture of alumina and potassium bisulphate. On taking up the mass with hot water small hexahedral crystals of anhydrous alum are obtained (Salm-Horstmar). This product is soluble, though slowly, in water, the following percentage solutions being obtained (Poggiale):—

Temperature.	$(SO_4)_3Al_2, SO_4K_2$ dissolved.	Temperature.	$(SO_4)_3Al_2, SO_4K_2$ dissolved.
0°	2·10	60°	26·70
10°	4·99	70°	35·11
20°	7·74	80°	45·66
30°	10·94	90°	58·68
40°	14·88	100°	74·53
50°	20·90		

The density of these solutions is given below:—

Sp. gr.	$(SO_4)_3Al_2, SO_4K_2 + 24H_2O$	Sp. gr.	$(SO_4)_3Al_2, SO_4K_2 + 24H_2O$
1·0065	1 per cent.	1·0218	4 per cent.
1·0110	2 ,,	1·0269	5 ,,
1·0166	3 ,,	1·0320	6 ,,

We have already seen that alum crystallises in octahedra; but there is a variety met with in commerce (Roman alum) as cubical crystals, and this kind was formerly preferred to all others by reason of its freedom from soluble iron salts. It is prepared from alunite, and only differs from ordinary alum in containing a slight excess of alumina (Leblanc).

A crystal of ordinary octahedral alum, if cut in the shape of a cube and placed in a solution of alum rendered basic by a little ammonia, will continue to grow, still retaining the cubical form; but if octahedral facets have been cut on the cube they will gradually disappear and the crystal will again become cubical. The converse, however, occurs if a solution of ordinary alum be employed.

De Hauer obtained hemihedral alum by cutting tetrahedron facets on a crystal of cubical alum and leaving it to grow in a solution of basic alum.

Ordinary alum may give rise to basic double sulphates, erroneously termed basic alum.

II. *Alunite.*—If caustic potash, soda, ammonia, or an alkali carbonate be added to a solution of alum a precipitate will be formed, which will re-dissolve on agitation, provided a slight excess of reagent has not been employed in the case of ammonia or the alkali carbonates. The originally acid reaction of the liquid will have become neutral, and on evaporating the solution at the ordinary temperature a crystalline incrustation, having the formula

$$SO_4Al_2O_2, (SO_4)_2Al_2O, SO_4K_2, 3H_2O$$

will be obtained.

When evaporated at 40° the formula of the precipitate will be $3(SO_4, Al_2O_2), SO_4K_2, 6H_2O$.

According to A. Mitscherlich, when a mixture of 3 grams of aluminium sulphate, 1 gram of potassium alum, and 10 c.c. of water is heated to 230°, rhombohedral crystals, with angles measuring 91·30° and 88·30°, and exhibiting the composition of alunite, will be formed.

Natural alunite is a very important mineral.

III. *Lœvigite.*—On boiling a concentrated solution of alum along with zinc, in a platinum capsule, hydrogen is liberated, and a crystalline product, having the formula $3(SO_4Al_2O_2), SO_4K_2, 9H_2O$, is obtained. This is lœvigite, and, according to Debray, the precipitate is almost insoluble in concentrated hydrochloric acid and nitric acid, but soluble in a mixture of equal parts, by weight, of water and sulphuric acid.

The same salt, but readily soluble in acids, has been obtained by Riffault by treating a solution of alum with caustic potash, avoiding any excess of the reagent; and the same worker also prepared it by boiling aluminium hydroxide in alum solution.

Walter Crum prepares lœvigite by heating a solution of alum with aluminium hydroxide or insoluble aluminium bi-acetate.

Mitscherlich has prepared it by heating a solution of ordinary alum to 230° in a sealed tube. It was this author who bestowed the name of lœvigite on the precipitate obtained by him, which gave the following composition :—

$$3(SO_4Al_2O_2), SO_4K_2, 9H_3O.$$

He also prepared it by heating potassium sulphate with aluminium sub-sulphate.

Lœvigite differs from alunite solely in that it contains a slightly higher percentage of water, which, however, it loses more readily when heated, and is further distinguishable from alunite by furnishing potassium sulphate, instead of alum, when subsequently taken up with water.

IV. *Roman Alum.*—This body, which has already been briefly referred to, only differs from ordinary alum by containing a slight excess of alumina and by crystallising in cubes. For a long time it constituted a very important industrial product, superior in many instances to ordinary alum by its freedom from soluble compounds of iron, and was prepared from alunite. It may easily be reproduced by adding a little ammonia or an alkali carbonate to a solution of ordinary alum heated to 30° or 40°, cubical alum crystallising out as the liquor cools down. When heated beyond 50° solutions of cubical alum deposit a little aluminium sub-sulphate, and the liquor on crystallising out will then furnish octahedral alum solely.

C. AMMONIUM ALUM. — I. *Ordinary variety* $(SO_4)_3Al_2$, $SO_4(NH_4)_2$, $24H_2O$.—This salt is used industrially in place of ordinary alum, and serves almost every purpose fulfilled by the latter. Both salts are produced in turn by alum manufacturers, the most weighty considerations influencing their production being the relative market price of the crystallising reagents, potassium sulphate and ammonium sulphate; at the present time the latter (" sulphate of ammonia ") being the cheaper, the balance is in favour of ammonium alum.

Great similarity exists between these two alums, both in appearance, crystalline habit (Fig. 17), and solubility.

When heated, ammonium alum melts and swells up like potassium alum ; and, like the latter, is also slightly efflorescent. Strongly heated, it leaves behind a residue of pure alumina.

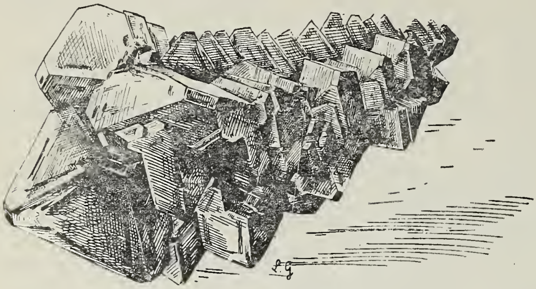


FIG. 17.—Block of alum.

The temperature required to render this decomposition complete is much higher than that necessary to secure the volatilisation of ammonium sulphate; consequently, if alum coated with ammonium sulphate be heated carefully, the latter can be volatilised without affecting the composition of the alum.

The sp. gr. of ammonium alum is 1·631.

The dehydrated alum is slightly less soluble in water than ordinary ammonium alum, 100 parts of water taking up (according to Poggiale)—

Temperature.	$(SO_4)_3Al_2, SO_4(NH_4)_2+24H_2O$ dissolved.	$(SO_4)_3Al_2, SO_4(NH_4)_2$
0°	5·22	2·63
10°	9·16	4·50
20°	13·66	6·57
30°	19·29	9·05
40°	27·27	12·35
50°	36·51	15·90
60°	51·29	21·09
70°	71·97	26·95
80°	103·08	35·19
90°	187·82	50·30
100°	421·90	70·83

The densities of ammonium alum solutions at 17·5° are given below, with the corresponding percentages of the dissolved salt :—

Sp. gr.	$(SO_4)_3Al_2, SO_4(NH_4)_2, 24H_2O$.	Sp. gr.	$(SO_4)_3Al_2, SO_4(NH_4)_2, 24H_2O$.
1·0060	1 per cent.	1·0200	4 per cent.
1·0109	2 ,,	1·0255	5 ,,
1·0156	3 ,,	1·0305	6 ,,

According to Mulder, the saturated solution boils at 110·6°, and contains 207·7 parts of alum, expressed as anhydrous alum.

II. *Basic Salts*—Just as, in the case of potassium alum, alunite and lœvigite are obtained, ammonium alum will also yield basic double salts.

When ammonia is added to a cold solution of alum there ensues a precipitate which re-dissolves on agitation, provided there is no excess of ammonia, the solution then containing the salt

$$(SO_4)_2Al_2O,\ SO_4(NH_4)_2,$$

which crystallises with difficulty.

According to Riffault, the addition of ammonia to a boiling solution of alum, until the precipitate becomes permanent, results in the formation of an ammoniacal lœvigite,

$$3(SO_4,\ Al_2O_2),\ SO_4(NH_4)_2,\ 9H_2O.$$

By keeping a mixture of ammonium sulphate, aluminium sulphate, and water at 190°, an alunite

$$3(SO_4,\ Al_2O_2),\ SO_4(NH_4)_2,\ 6H_2O,$$

analogous to potassium alunite, is obtained.

Ammonium alum is found to a small extent in nature.

D. SODIUM ALUM, $(SO_4)_3Al_2,\ SO_4Na_2 + 24H_2O$, may be prepared by crystallising a solution containing equivalent quantities of aluminium sulphate and sodium sulphate. It has the same crystalline form as ordinary alum, but is very efflorescent, the crystals turning to powder at the end of a few days.

According to Buignet, the sp. gr. of sodium alum is 1·567. It is very soluble in water, 100 parts of water at 16° taking up 110 parts of the salt. For this reason sodium alum cannot be separated, on a manufacturing scale, from sulphate of iron, and therefore ferruginous materials are unsuited for the preparation of this alum.

Solutions of sodium alum are very easy to supersaturate. If a solution of this salt be concentrated by evaporation to a point at which it begins to solidify on cooling, it will be found that large crystals form on the addition of a little water, the entire mass crystallising from the surface downwards. The change is facilitated by stirring.

Sodium alum is insoluble in alcohol. It occurs in nature as mendozite.

15. **Aluminium Dithionate** is obtained by decomposing barium dithionate with aluminium sulphate, but is for the most part decomposed during the evaporation of the solution.

16. **Aluminium Nitride** (Al_2N_2).—This body occurs in the crystalline form as short orthorhombic prisms with dihedral apices. In the amorphous condition it is pale yellow, while the crystals are translucent and of a honey-yellow colour.

It was obtained by Mallet in various experiments, wherein aluminium was raised to a high temperature in a carbon crucible. The surface of the metal exhibited yellow crystalline particles, which were liberated, by dilute hydrochloric acid, along with an amorphous mass of the same colour. The nitrogen was evidently derived from the air traversing the crucible walls. The nitride was always accompanied by a little crystalline alumina.

To obtain a sufficient quantity for examination, Mallet heated aluminium to a very high temperature with dry sodium carbonate, in a carbon or lime crucible contained in a second crucible of graphite, the space between the two vessels being packed with lampblack.

When calcined in contact with air this body slowly yields up its nitrogen, and the aluminium oxidises. In presence of moist air it decomposes spontaneously, alumina being formed and hydrogen evolved. The amorphous nitride is less stable than the crystalline form.

17. **Aluminium Nitrate** ($Al_2(NO_3)_6$, $2H_2O$) is obtained by dissolving aluminium hydroxide in nitric acid. The solution is evaporated, care being taken that the liquid contains an excess of acid; and, on re-cooling, large crystals are deposited, which contain 15 molecules of water. When crystallised in concentrated nitric acid, only 2 molecules of water are retained.

Aluminium nitrate is a very deliquescent salt. At about 140° it decomposes into alumina and nitric acid; and this property has been utilised in analysis for the separation of aluminium from calcium and magnesium.

The crystals of aluminium nitrate melt at 72·8° to a colourless liquid, which solidifies on re-cooling, the mass having a crystalline texture. They are soluble in water, nitric acid, or alcohol.

18. **Aluminium Phosphates.**—These are three in number, derived from

PO_4H_3 . . .	Orthophosphoric acid,
$P_2O_7H_4$ . . .	Pyrophosphoric „
PO_3H . . .	Metaphosphoric „

A. ALUMINIUM ORTHOPHOSPHATE, $(PO_4)_2Al_2$.—This salt is prepared by precipitating a neutral solution of alumina with ordinary sodium phosphate, and comes down as a white gelatinous substance, which, when dried in the air, retains 9 molecules of water (Rammelsberg). According to the results obtained by different workers, the content of water varies and does not appear to be very constant.

The salt prepared as above is soluble in caustic potash, but insoluble in acetic acid. This property, which is shared by ferric phosphate, enables these two to be easily separated from the phosphates of lime, magnesia, etc.

When phosphoric acid is added to a concentrated solution of sodium aluminate until the reaction is acid, and the mixture is then heated to 250° under pressure, the salt $(PO_4)_2Al_2$ is obtained as hexagonal prisms, of sp. gr. 2·59, infusible at red heat, insoluble in HCl, HNO_3, and soluble (though with difficulty) in concentrated H_2SO_4. By heating dissolved alumina in phosphoric acid, Hautefeuille and Margottet obtained—

At 100°, the salt Al_2O_3, $3P_2O_5$, $6H_2O$, crystallising in colourless prisms;
At 150° to 200°, the salt Al_2O_3, $3P_2O_5$, $4H_2O$, in needles;
Above 200°, the salt Al_2O_3, $3P_2O_5$, crystallising in regular tetrahedra.

According to Rammelsberg, the addition of ammonia to an acid solution containing aluminium phosphate results in the formation of a basic salt,

$$4(Al_2O_3),\ 3(P_2O_5),\ 18H_2O,$$

which phosphate, combined with the aluminium fluoride, forms the native mineral wavellite, the composition of which is given by Berthier as

$$Al_2F_6, [(Al_2O_3)_4, (P_2O_5)_3]_3, 36H_2O.$$

On boiling a mixture of dissolved aluminium sulphate and ordinary ammonium phosphate in presence of a little sulphuric acid, there results, according to Millot, an acid phosphate,

$$2(PO_4)_3Al_2H_3 + 17H_2O.$$

This compound, when treated by phosphoric acid in suitable amount, furnishes a residue which, when washed and analysed, yields values corresponding to the formula

$$(PO_4)_4Al_2H_6, 5H_2O.$$

By precipitating with ammonia an acid solution of one of the foregoing phosphates, avoiding an excess of the reagent, Millot obtained a basic phosphate,

$$2(PO_4)_2Al_2, Al_2O_3, 8H_2O.$$

B. ALUMINIUM PYROPHOSPHATE is obtained as a white amorphous precipitate soluble in mineral acids, sodium pyrophosphate solution, ammonia, etc., by neutralising sodium pyrophosphate with aluminium chloride solution.

It may also be prepared, this time as very fine clinorhombic crystals, by treating aluminium metaphosphate with fused metaphosphoric acid containing a certain quantity of tribasic silver phosphate (Hautefeuille and Margottet).

C. ALUMINIUM METAPHOSPHATE.—Hautefeuille and Margottet obtained this salt by treating alumina with fused metaphosphoric acid. On treating the mass with boiling water, aluminium metaphosphate is obtained in the form of cubic crystals exhibiting modifications tending towards the octahedron, rhomboid dodecahedron, or trioctahedron. Nevertheless, when this method of preparation is adopted, the crystals are for the most part badly formed, being softened by the temperature necessary for fusing the metaphosphoric acid. Fine, large crystals, free from silver, may, however, be obtained by adding to the mass a small quantity of triargentic phosphate, which imparts fluidity to the metaphosphoric acid.

If the proportion of triargentic phosphate is at all large, and particularly when 2 parts of alumina are added to a mixture of 4 to 6 parts of metaphosphoric acid and 8 parts of triargentic phosphate; or if crystals of aluminium metaphosphate be treated with about 3 times their own weight of triargentic nitrate, the crystals obtained are colourless, perfectly transparent, double refracting, act energetically on polarised light, and are derived from an orthorhombic prism. Their formula is $2Al_2O_3$, Ag_2O, $4P_2O_5$.

A slight excess of metaphosphoric acid gives rise to clinorhombic crystals of aluminium pyrophosphate, whilst an excess of triargentic phosphate produces pointed octahedra, apparently derived from a clinorhombic prism, and corresponding to the formula $2Al_2O_3$, $3P_2O_5$.

Aluminium phosphate occurs in nature, most frequently as a double phosphate (wavellite, amblygonite, childrenite, turquoise).

19. **Aluminium Arsenite.**—This salt may be obtained by precipitating aluminium sulphate with barium arsenite and concentrating the filtrate—at first by gentle heat, and afterwards over sulphuric acid. It crystallises in fine rhombohedral octahedra. On concentrating the solution of these crystals, at 70°, arsenious acid is formed, a basic arsenite remaining in solution.

20. **Aluminium Arsenates.**—Coloriano obtained the arsenate $(As_5O_4)_2$, Al_2, as lenticular crystals, by heating a solution of trisodic arsenate and aluminium sulphate to 200°. The "neutral arsenate" of Berzelius, $(As_2O_7)_3Al_4$, was the pyro-arsenate. Probably this salt is hydrated and corresponds to

$$\left.\begin{matrix} Al_2^{\text{VI}} \\ H_3 \end{matrix}\right\} (AsO_4)_3.$$

It is insoluble, but there is a very soluble acid salt which cannot be crystallised, and probably corresponds to the formula

$$\left.\begin{matrix} Al_2^{\text{VI}} \\ H_6 \end{matrix}\right\} (AsO_4)_4.$$

21. **Aluminium Silicates.**—In nature these silicates occur in considerable quantities, and constitute diosthene, the felspars, kaolins, clays, etc. Fuller details of these rocks will be given in dealing with aluminium minerals. Double silicates of this metal are also easily produced, and are in fact the most frequent form of occurrence.

By exposing an intimate mixture of 4 parts kaolin and 3 parts common salt to a cherry-red heat, Gorgeu obtained a double silicate of aluminium and sodium, $2SiO_2$, Al_2O_3, Na_2O. The same author also prepared the double silicate of aluminium and potassium, $2SiO_2$, Al_2O_3, K_2O, by heating 1 part of kaolin with 2 parts of potassium iodide in a covered platinum crucible for 2 hours. The resulting salt is amorphous, insoluble in water, and retains 2 per cent. of iodide.

These double silicates are soluble in hydrochloric acid and dilute nitric acid, but insoluble in alkalis or carbonates; and are infusible, or nearly so, at a bright-red heat.

When 1 part of kaolin, $2SiO_2$, Al_2O_3, $2H_2O$, and 13 parts of sodium carbonate are heated together, it will be found that carbon dioxide is evolved at a cherry-red heat, and again when the temperature approaches orange-red heat. Consequently there are two successive reactions, and these give rise to different silicates, the first corresponding to the formula

$$3SiO_2, 2Al_2O_3, 3NaO,$$

whilst the second approximates to

$$SiO_2, AlO_3, Na_2O.$$

The action of fused caustic soda on kaolin is very rapid.

§ 3. ALUMINIUM MINERALS

Aluminium is met with very abundantly in nature, in the form of numerous compounds, the most important of which belong to the silicate series of minerals.

Many of these compounds, whether silicates, oxides, hydroxides, or sulphates, etc., have found extensive application, and are utilised by the jeweller and in various industries. The most interesting of these bodies will now be examined.

22. **Minerals containing Fluorine.**—*A*. FLUELLITE.—White, vitreous, crystalline incrustations, found on Stenno-Gwyn quartz (Cornwall), and consisting of aluminium fluoride. This mineral belongs to the third degree of hardness, and crystallises in orthorhombic octahedra $a'a' = 109^\circ\ 6'$ and $82^\circ\ 12'$.

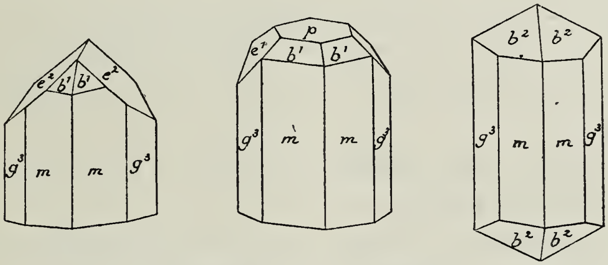
B. TOPAZ, $SiO_4(Al_2F_2)$, (syn.: Chrysolite, physalite, pyrophysalite, pycnite).

Occurs as honey-yellow, brownish, reddish, bluish, or colourless crystals in gneiss and granite, associated with tourmaline, mica, or emerald; frequently also with apatite, fluorine, cassiderite, etc.; or in talc rocks or mica schist.

The principal deposits are in the Ural and Brazil.

Topaz is slightly attacked by H_2SO_4, hydrofluoric acid being liberated. In the blast furnace it parts with silicon fluoride, without fusing. Tested with cobalt nitrate, it gives the reaction for alumina.

The hardness of these crystals is 8, the sp. gr. 3·4 to 3·6, and the crystalline form that of orthorhombic prisms. See Figs. 18, 19, 20.



FIGS. 18, 19, and 20.—Topaz.

C. CRYOLITE is a double fluoride of aluminium and sodium, Al_2F_6, $6NaF$. It is found as fragile, whitish, crystalline masses cleaving in three rectangular directions, and occurs in Greenland and the Ural.

Sulphuric acid decomposes cryolite, liberating HF. It is very fusible; has a sp. gr., 2·9 to 3·7; hardness, 2·5; and crystallises in the anorthic system.

23. **Anhydrous Aluminium Oxide Minerals** (Al_2O_3).—*A.* CORUNDUM.—This mineral is a pure, crystalline sesquioxide of aluminium, colourless, and crystallising in the rhombohedric system. The primitive rhombohedron (86·4°) is, however, rare, and the mineral is mostly found in basal hexagonal prisms d_1a_1, frequently terminating in pyramids.

The hardness is 9; the sp. gr. ranges from 3·9 to 4·2;

refractive power, 0·739. It exhibits double refraction at one negative axis.

Corundum is unacted on by acids and is infusible in the blast furnace. Owing to its hardness and high refractive power, it forms a highly precious stone for the jeweller.

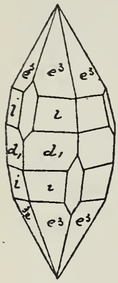


Fig. 21.
Corundum.

In addition to the colourless variety, corundums are met with containing traces of the oxides of iron, chromium, or titanium, and forming coloured gems, each of which has its distinctive name.

Tinged with red by traces of chromium oxide, it constitutes the *oriental ruby*, which is more valuable than the diamond. The finest specimens come from Ceylon, India, and China.

Coloured blue, it forms the *sapphire*, varying in shape from dark to very light blue, and less valuable than the ruby.

The green corundum, or *emerald*, is very rare, and is found in Ceylon.

The *oriental topaz* is yellow corundum. It is of lower value than the preceding gems.

Violet corundum, or *oriental amethyst*, is somewhat rare.

A considerable quantity of corundum is found in France, in the extinct volcanoes of Auvergne; but the mineral is of no value, the crystals being devoid of transparence.

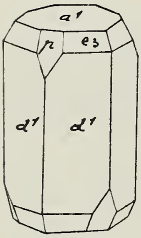


Fig. 22.
Corundum.

Emery is a mixture of corundum and ferric oxide, the latter often attaining 30 per cent. It is a dark coloured mineral, two types of which are met with—the compact and the granular—frequently containing quartz, chlorite, etc.

Emery is found in beds or stratified deposits among gneiss rocks and mica schists, in Saxony, China, India, and, above all, in Asia Minor, the first deposit having been found in the latter region at Gumuch-Dagh, near the ancient city of Magnesia.

On account of its hardness this mineral is employed for polishing hard substances, metals, etc.

24. **Aluminium Hydroxide Minerals.**—*A.* DIASPORE (Al_2O_3, H_2O).—Diaspore is generally found with corundum in dolomite, chloritic schists, etc.; and has been discovered in gneiss at Bournac (Haute-Loire). It crystallises in the orthorhombic system; generally as orthorhombic prisms (*mm.* 129° 47′), truncated at g^1, and terminating in a octahedron $b_1b_1 = 151° 34′$. The line of cleavage is along g^1 or, less frequently, *m.* Degree of hardness, 6·5 to 7; sp. gr., 3·2 to 3·5; colour white or yellowish white. It is transparent, and exhibits a very brilliant, conchoidal fracture.

Heated in a sealed tube, diaspore decrepitates violently, and forms white, pearly scales. At a high temperature water is liberated. Tested with cobalt nitrate, it gives a fine blue coloration. In its ordinary state it is unacted upon by acids, but loses its resistance when calcined.

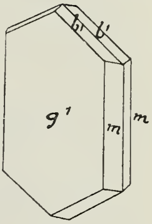


FIG. 23.
Diaspore.

B. BAUXITE (Al_2O_3, $2H_2O$).—This mineral is sometimes compact, sometimes oolitic, and occurs as concretionary rounded grains or as earthy masses. The colour is variable: white, grey, yellow, red, brown, etc., and the mass is hard, brittle, and more and more tinged with red as the content of ferric oxide increases. The following table gives the results yielded by different varieties of this mineral on analysis (Pommier):—

Constituents.	Bauxite.				
	Rose.	Yellow with Brown Veins.	Light Red.	Brown Red.	Dark Brown.
Alumina	66·82	54·10	53·00	44·40	44·10
Ferric oxide . . .	1·92	10·40	24·20	30·30	37·20
Silica	16·26	12·00	7·50	15·00	4·70
Lime	...	...	1·50	...	...
Water	15·00	24·90	13·10	9·79	12·00

Other samples analysed at the Ecole des Mines gave—

Constituents.	Bauxite.		
	White.	Rose.	Red.
Silica	8·30	10·20	15·00
Alumina	75·70	52·50	35·30
Ferric oxide	1·90	24·60	27·90
Lime	0·30	0·35	0·38
Magnesia	0·18	0·27	0·36
Loss on calcination	13·50	12·00	11·00

It is thus evident that bauxite is a mineral of extremely variable composition. Only the purest kinds are utilised industrially, since, for the manufacture of aluminium sulphate in particular, freedom (as far as possible) from iron is essential; and it is on this account that consumers lay down a maximum percentage of ferric oxide, which must not be exceeded in the goods supplied by sellers. According to Lacarrière, the bauxite treated in his works at Noyon contains on an average—

Constituents.	Villevayrac Bauxite.
Alumina	63·00
Ferric oxide	2·90
Calcium carbonate	5·10
Insoluble in H_2SO_4	10·50
Loss at red heat	19·00

The permissible maximum of ferric oxide is fixed at 3 per cent., and the minimum content of alumina at 60 per cent.

Bauxite was discovered by Berthier, at Baux near Arles, in the form of grains disseminated in compact chalk; it is also found at Revest near Toulon, at Allauch (Var), etc.

Far from being of restricted accidental occurrence, bauxite forms numerous isolated deposits in the cretaceous system, about a line drawn from Tarascon to Antibes, for a distance of over

90 miles. It has been discovered and worked by Augé, of Montpelier, at Villevayrac (Hérault), and other deposits are known to exist in Senegal, Calabria, Ireland, Austria, etc.

The mineral is extracted by open workings, or underground headings, the ground being broken and the bauxite mined by blasting. The crude product is hand-picked and pulverised before being used.

Among the numerous applications to which the bauxite is put are: the manufacture of sodium aluminate, pure alumina, aluminium, aluminium sulphate, alums, etc.

25. **Aluminates.**—These minerals belong to the group of spinels, the general formula of which is MR_2O_4; $M = Mg$, or Fe, Zn, Mn; and $R = Al$, Fe, Mn, Cr, Ti, etc. They usually crystallise in cubes.

A. SPINEL RUBY (balas ruby) ($MgAl_2O_4$).—This occurs in more or less modified octahedra. The fracture is conchoidal; the lustre vitreous; colour variable, but generally red; sp. gr. varies between 3·5 and 3·8; hardness, 8. It is infusible in the blowpipe flame; only slightly soluble in borax; soluble in sodium-ammonium phosphate.

When containing variable quantities of ferric oxide, spinel ruby is generally black, and is known as *ceylanite*, *pléonaste*, *chlorospinel*, etc. Associated with chrome, it is yellow or greenish yellow, and is then termed *picotite*.

Red, rose, and violet spinels are employed by the jeweller, but are held in less esteem than the oriental ruby.

Spinels are found in crystalline chalk rocks, gneiss, and serpentine, and are often associated with the oriental ruby. Pléonaste is found in the cipolines situated in the gneiss of Mercus and Arignac, to the north of Tarascon; and also as grains disseminated in herzolite, near Montpelier.

Gahnite is a zinciferous spinel.

B. CYMOPHANE ($GlAl_2O_4$), (syn.: Chrysoberyl; oriental chrysolite).—A glucinum aluminate crystallising in the orthorhombic prism system, generally in the form of tabular crystals of hexagonal shape (Fig. 24).

Cymophane is greenish white, verging on grey, in colour;

trichroic, opalescent, and non-transparent; sp. gr., 3·75; degree of hardness, 8·5.

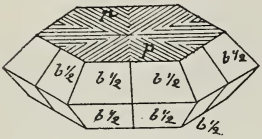


FIG. 24.—Cymophane.

A green variety, found in Ceylon, is known as cat's-eye, on account of its peculiar sheen.

Cymophane is found in granite, gneiss, mica schist, etc.

26. **Sulphatic Minerals.**—*A.* ALUNOGEN ($Al_2(SO_4)_3$, $18H_2O$), (syn.: Feather alum, halotrichite, etc.).

Alunogen is monoclinic, and constitutes fibrous or scaly masses found in solfatara. It is translucent and very soluble; the degree of hardness is 1·5 to 2, and the sp. gr. 1·6 to 1·8. It has been found in the bitumen deposits at Chamalières.

B. ALUMIANE consists of anhydrous aluminium sulphate, and has been found in the Sierra Almagrera mines. It is white, and occurs as a vitreous mass or in microscopic crystals. The degree of hardness is 2 to 3, and the sp. gr. 2·70 to 2·78.

C. WEBSTERITE, (syn.: Aluminite, hallite, etc.) ($SO_4(Al_2O_2)$, $9H_2O$).—This mineral is a hydrated sub-sulphate of aluminium, occurring as kidney-shaped earthy masses, dull white in colour, tender, soft to the touch, and biting to the palate. It is soluble in acids, gives off water when heated, and produces a fine blue colour in the cobalt nitrate test.

Websterite is met with in the lower tertiary formation, as veins or nodules in plastic clay, at Auteuil, Halle, New-Haven, etc.

D. ALUMS.—Potassium alum occurs as an efflorescence, or as fibrous masses, in aluminous schists; sodium alum, as fibrous crusts in the sulphur springs of Naples, Milo, etc.; ammonium alum, in lignite, at Tschermig (Bohemia), and in the crater of Mt. Etna.

E. ALUNITE, (syn.: Alkaline sub-sulphate of alumina, alum stone, etc.) (K_2O, $3Al_2O_3$, $4SO_3$, $6H_2O$). There are four separate types of this mineral: the compact, the porphyroid, the earthy, and the breccial.

Alunite is a rock of whitish, greyish, yellowish, or reddish colour, found at La Tolfa near Civita Vecchia; at Montioni in the Duchy of Piombino; at Mursaly, Munkact, and Tokay in

Hungary; in the islands of Milo, Argentino, and Nipoglio (Grecian Archipelago); at Puy-de-Sancy and Madriat (Auvergne); Samsoun in Asia Minor, and in Australia.

It is sometimes met with crystallised in rhombohedra, but more frequently as a light greyish rock, as hard as quartz and with an average sp. gr. = 2·5.

In the blowpipe flame alunite decrepitates but declines to fuse; it gives off water in a closed tube. The degree of hardness is 3·5 to 4; sp. gr., 2·6 to 2·75. It is soluble in H_2SO_4, and is partly soluble in water after calcination.

At La Tolfa the mineral occurs in limited deposits in the midst of reddish argillaceous schists of the Jurassic epoch.

The deposit at Madriat is about 15 square kilometres (6 square miles) in area, to the south-east of the Mt. Dore range (Issoir district), and occurs, disseminated in the form of balls, kidney-shaped masses, etc., in blood-red clays of the lower tertiary formation.

The composition of alunite is exceedingly variable, the following analyses (Pommier) showing the percentage constitution of the Madriat mineral:—

Constituents.	Alunite.			
	White.	Rose.	Red.	Dark Red.
Potash	10·6	6·3	7·5	4·0
Alumina and ferric oxide	36·3	38·1	38·3	39·8
Lime	1·9	2·4	2·1	2·6
Silica	2·3	13·4	11·0	17·3
Sulphuric acid	34·7	23·9	25·2	19·7
Water	14·5	14·6	14·6	16·1

Vauquelin gives the following analysis of Mt. Dore alunite:—

Silica	28·40
Sulphuric acid	27·03
Alumina	31·80
Potash	5·79
Ferrous oxide	1·44
Water	3·72
Loss	1·82

According to Pommier, La Tolfa alunite consists of:—

Constituents.	1	2	3
Sulphuric acid	25·00	16·50	27·63
Alumina	43·92	19·00	26·29
Potash	3·08	4·00	7·17
Water	4·00	3·00	12·04
Silica	24·00	56·50	...
Silicates	...	...	23·59
Unestimated	...	...	3·28

Further analyses by different chemists give the following composition of alunites from various sources:—

Constituents.	La Tolfa.	Zabrze.	Zabrze.	Montione.
	(Stein.)	(Löwig.)	(Mitscherlich.)	(Descotils.)
Sulphuric acid	37·50	34·84	34·81	35·60
Alumina	35·00	33·37	34·95	40·00
Ferric oxide	2·10	...	0·68	...
Potash	8·00	10·10	9·30	13·80
Soda	...	...	0·39	...
Water	14·50	18·32	17·88	10·60
Silica	1·90	3·37*	0·26	...
Remainder	...	...	1·74†	...

* Including organic matter.

† Magnesia, 0·55; lime, 0·28; baryta, 0·44; organic matter, 0·47.

Constituents.	La Tolfa.		Beregszaz, Hungary.	Maszai, Hungary.	Gleichenberg, Styria.	Pic-de-Sancy, Puy-de-Dome.
	(Vauquelin.)	(Mitscherlich.)	(Klaproth.)	(Mitscherlich.)	(Fridau.)	(Cordier.)
Sulphuric acid	25·00	27·63	12·50	27·10	16·50	27·00
Alumina	43·92	26·29	17·50	28·82	19·06	31·80
Ferric oxide	...	...	...	...	1·13	1·40
Potash	3·08	7·17	1·00	...	3·97	5·80
Water	4·00	12·04	5·00	...	7·23	3·70
Silica	24·00	...	62·25	28·10	50·71	28·40
Silicates	...	23·59	...	...	...	...
Remainder	...	3·28*	...	15·85†	1·40‡	...

* Magnesia, 3·21; lime, 0·7.

† Including 0·13 of barium and unestimated matters.

‡ Lime, 0·56; magnesia, 0·41; magnesium sulphate, 0·9; magnesium chloride, 0·03; potassium silicate, 0·31.

The following analyses of the same mineral are given by Vivien (1), Cordier (2), and Klaproth (3).

Constituents.	1 (Vivien.)	2 (Cordier.)	3 (Klaproth.)
Potash	7·77	10·021	4·00
Alumina	37·00	39·654	19·90
Sulphuric acid	40·17	35·495	16·50
Ferric oxide	1·70	...	...
Water, etc.	13·36	14·830	3·00
Silica	...	...	36·50

For the sake of comparison the mean composition of crude La Tolfa alunite, treated for aluminium sulphate, is given below:—

Potassium sulphate	14·00
Alumina	28·00
Sulphur trioxide	20·00
Ferric oxide	2·00

Alunite is worked on a large scale for the manufacture of alum and aluminium sulphate, for which purpose it was utilised as far back as the fifteenth century.

F. LOEWIGITE is also a hydrated sulphate of alumina and potash, SO_4K_2, $3(SO_4Al_2O_2)$, $9H_2O$, and is found in rounded masses, resembling compact alunite, at Zabrze (Silesia) and La Tolfa. Before the blowpipe it exhibits the same characteristics as alunite. The degree of hardness is 3 to 4; the sp. gr., 2·6; fracture, conchoidal.

27. **Phosphatic Minerals.**—*A.* WAVELLITE, $(PO_4)_2$, $(Al.OH)_3$, $4\frac{1}{2}H_2O$.—Wavellite crystallises according to the orthorhombic system, the crystals being frequently acicular and grouped in radial, spherical, or hemispherical masses. Occasionally they occur as small greenish prisms. The colour is variable: grey, green, yellow, etc. Cleavage is easy, and the fracture is imperfectly conchoidal; degree of hardness, 3·5 to 4; sp. gr., 2·32 to 2·34.

Before the blowpipe wavellite swells up, and gives the aluminium reaction with cobalt nitrate. It is soluble in acids and caustic potash, and contains fluorine.

Occurrence.—In the fissures of Devonshire clay shales; in the brown hæmatite contained in Jurassic chalk at Amberg (Bavaria); in stanniferous veins at Montebras (Creuse), at Saint-Girons (Ariège); and in America.

B. TURQUOISE, $(PO_4)Al_2(OH)_3H_2O$.—Turquoise exhibits a microcrystalline structure and a conchoidal or irregular fracture; the colour is azure blue, apple green, etc., and the lustre faintly vitreous. Degree of hardness, 6; sp. gr., 2·6 to 2·8. The powdered mineral is white or greenish, and cupric oxide is present to the extent of 2 to 5 per cent.

Turquoise is infusible before the blowpipe, to the flame of which it imparts a green tinge. Heated in a closed tube, it decrepitates, gives off water, and becomes black or brown. It is soluble in acids; and, in presence of sodium ammonium phosphate, furnishes a copper-red bead when heated in the reducing flame.

Turquoise is used by the jeweller, the most highly esteemed kind coming from Nichapour in Persia, where it is found in veins over a clay schist. It has also been found at Hölsnitz (Saxony), Mt. Sinai, Suez, and Simorre (Gers).

28. **Silicates.**—Alumina occurs as a constituent of a large number of multiple silicates, the most important mineral of this class being the clays and felspars.

A. CLAYS.—This term is applied to a large number of amorphous substances, derived from the decomposition of other minerals and bearing a number of distinctive names.

The clays are all hydrated aluminium silicates, more or less pure, and attackable by acids; and are divided into four classes:—

I. Clays proper, or potters' clays, prepared by sedimentation.

II. Kaolins, produced by the decomposition, *in situ*, of felspathic rocks.

III. Smectic clays, and clays produced by chemical decomposition.

IV. Boles and ochres.

I. *Clays properly so called.*—The sp. gr. of these bodies varies between 1·7 and 2·7. They form white, grey, yellow, or black masses, exhibiting an earthy fracture, biting to the tongue, and mixing with water to a plastic paste. On exposure to dry air they lose a portion of their moisture, and undergo considerable shrinkage; the whole of the water is given off on calcination, the shrinkage increasing with the temperature. Heated to whiteness, they become sufficiently hard to stand fire.

These clays are acted upon to some extent by boiling hot hydrochloric and nitric acids, and more extensively by sulphuric acid. They are infusible before the blowpipe.

The subjoined analyses by Berthier represent typical examples of these clays:—

	Dreux clay.	Forges clay.
Silica	50·60	65·00
Alumina	35·20	24·00
Ferric oxide . . .	0·40	traces
Water	13·10	11·00

Marl is clay containing 20 to 25 per cent. of chalk.

II. *Kaolin* is a very pure clay resulting from the decomposition of felspar, and is usually mixed with fragments of the parent rock, mica, quartz, etc., from which it is purified by levigation.

Constituents.	Kaolin from									
	St. Yrieix.		Sy-Kang (China).	Tong-Kong (China).	Loch-karewska.	Sosa.	Aue.	Passau.	Plympton (Devon).
Silica . . .	36·25	48·68	55·30	50·50	46·75	45·07	35·89	45·34	44·26
Alumina . .	33·35	36·92	30·30	33·70	34·98	38·15	34·12	35·18	36·81
Lime . . .	...	...	...	...	1·25	...	...	1·55	2·72
Magnesia . .	2·40	0·52	0·40	0·80	0·48	1·80	0·69		
Potash . . .	...	...	1·10	1·90	0·29	...	...	...	...
Soda . . .	...	0·58	2·70	...	1·34	...	...	...	...
Ferric oxide . .	...	...	2·00	...	...	...	...	...	...
Water . . .	12·00	13·13	8·20	11·20	13·70	9·69	11·09	17·24	12·74

Pure kaolin is white, unctuous to the touch, and has a sp. gr. of 2·21 to 2·26. It is attacked by hot sulphuric acid, but is infusible, or nearly so, before the blowpipe.

Amphigene and emerald may become converted into kaolin.

The preceding table gives the composition of kaolins from various sources.

III. *Smectic Clays.*—These constitute beds intercalated among oolithic and cretaceous rocks. They are translucid at the edges; white, brown, or variegated; biting to the tongue; mix with water to form a short paste; and absorb fats. They are attacked by acids, and fuse to a greyish enamel before the blowpipe. The sp. gr. varies between 1·7 and 2·4.

The "fossil flour" of the Chinese is white and earthy, exhibiting an aromatic odour; it contains 0·002 per cent. of nitrogen, and is said to possess alimentary properties.

Halloysite is a compact clay, with translucent edges and a waxy sheen; it is of various colours, and is met with in veins and deposits.

This clay dissolves to a jelly in acids, infusible before the blowpipe, and has a sp. gr., 1·92 to 2·12.

Lithomarge is somewhat similar to halloysite.

Allophane is a variety usually occupying irregular cavities in beds of limonite and chessylite.

The composition of these clays is shown in the following table:—

Constituents.	Clay from Conde.	Halloysite from Angleur.	Allophane from Firmy.
Silica	43·00	44·94	23·76
Alumina	32·50	39·06	39·68
Ferrous oxide	1·20	...	...
Cupric oxide	...	...	0·65
Magnesia	0·30	...	...
Lime	1·02	...	...
Soda and potash	0·40	...	...
Water	21·70	16·00	35·49
Gelatinous silica	1·50	...	...

IV. *Boles and ochres* are argillaceous substances containing a large proportion of ferric oxide, and exhibiting an earthy fracture. They are opaque, brown, red, or yellow; biting to the tongue, and crumbling in water.

Boles and ochres are partly attacked by acids; the sp. gr. varies between 1·6 and 2·5, and the degree of hardness from 1·5 to 2. Certain of these bodies are employed as pigments, either in the raw state or when calcined, *e.g.*, sienna, umber, and sinope.

The composition of two of them is given below :—

	Säsebühl Bole.	Amberg Ochre.
Alumina	20·90	14·21
Silica	41·90	33·23
Ferric oxide . . .	12·20	37·76
Magnesia	...	1·38
Water	24·90	13·24

Other bodies that must also be included in this group are the unctuous, canary yellow, hydrated silicate known as *nontronite*, from Nontron (Dordogne), Montmort, and Autun (Saône-et-Loire), as well as the chromiferous clays: *chrome ochre* (from around Creusot), which imparts a green colour to triassic arkose rocks, and *wolkouskoite*, a pigmentary earth found in the province of Perm (Russia).

The clays are employed in the production of ceramic ware, porcelain, etc.; the more aluminous kinds, especially kaolin, are largely utilised for the manufacture of aluminium sulphate.

B. ANDALUSITE (syn.: Apyrous felspar) is an aluminium silicate, $Al_2SiO_5 = Al_2O_3SiO_2$, found in almost square rhomboidal prisms, covered, and even penetrated, by mica and disthene, and occurs in crystalline schists.

Andalusite is opaque, and grey or rosy in colour; a transparent, greenish-yellow, polychroic variety is met with in Brazil.

It is unattacked by acids; infusible before the blowpipe; the degree of hardness is 7·5; and the sp. gr., 3·16 to 3·20. The crystals belong to the orthorhombic prism system.

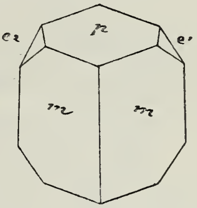


FIG. 25.—Andalusite.

C. FELSPARS.—The felspars occupy an important place among the constituents of the eruptive rocks. They are colourless or white, and only assume a greenish or rose coloration when they have undergone alteration; they are often transparent.

The distinctive characteristic of the felspars consists in the existence of two planes of cleavage, at an angle of 87° to 90°. The degree of hardness is 6 to 7, and the sp. gr. 2·4 to 2·8.

All felspars are silicates of aluminium and an alkali metal, such as potassium or sodium, or an alkaline earth, *e.g.*, lime and occasionally barium. The proportion of the oxygen combined with the alumina is always as 3 : 1 compared with that attached to the other bases. As for the oxygen in the silica, its proportion is essentially characteristic of the different kinds of felspar.

The entire series of felspars may be regarded as polysilicates, each member of which differs from its preceding neighbour by one additional molecule of silica.

The following table gives a classification of the felspars in the order of their increasing richness in silica:—

	Ratio of Oxygen.				
	R_2O or RO		Al_2O_3		SiO_2
Anorthite	1	:	3	:	4
Labradorite	1	:	3	:	6
Andesine	1	:	3	:	8
Oligoclase	1	:	3	:	10
Albite	1	:	3	:	12

I. *Anorthite* ($Si_2O_8Al_2Ca$).—The only occurrence of this felspar as decided crystals is in the volcanic rocks in certain localities, such as the ejected blocks of Somma, the lavas of Iceland, in Java, etc. In France it is met with as laminar masses in certain galbros (St. Clement, Puy-de-Dome), pyroxerite (Roguedon, Morbihan), or diorite (Corsican orbicular diorite). Some varieties are rose or rosy grey in colour.

This felspar is completely attacked by acids, a deposit of silica being left. Before the blowpipe it fuses to a vesicular glass. The degree of hardness is 6; the sp. gr., 2·69 to 2·75; and the crystals belong to the anorthic prism type, $mt = 120^\circ\ 30'$; $pm = 111^\circ\ 40'$; $pt = 114^\circ\ 7'$.

II. *Labradorite* ($Si_3O_{10}Al_2Ca$) is but very rarely met with in the form of crystals, being generally found as white lamellar masses in diorites, diabases, euphotides, norites, etc. The finest specimens come from Labrador, where they form a rock with hypersthene and amphibole.

The crystalline form of labradorite is the anorthic prism, $mt = 121^\circ\ 37'$; $pm = 110^\circ\ 50'$; $pa = 98^\circ\ 58'$. Hydrochloric acid attacks it with difficulty. Before the blowpipe it fuses quickly to a colourless glass. The sp. gr. is 2·67 to 2·76.

III. *Andesine* ($Si_4O_{12}Al_2R$) ($R = Ca$ or Na_2).—This substance forms milk-white crystals in Esterel blue porphyry (dacite), and laminar masses in Autun gneiss. The crystalline form is that of the anorthic prism, $mt = 120^\circ$; $pg^1 = 86^\circ\ 10'$; $pt = 115^\circ$.

It is imperfectly attacked by acids, and is somewhat infusible before the blowpipe, the edges alone melting to a milky glass.

IV. *Oligoclase* ($Si_5O_{14}Al_2Na_2$) is rarely met with in the state of crystals, being generally found as white or greenish laminar masses, in granite, syenite, porphyry, basalt, etc.

It fuses with difficulty before the blowpipe, and is almost unacted upon by acids. The degree of hardness is 6; sp. gr., 2·63 to 2·73; and the crystalline form that of the anorthic prism, $mt = 120^\circ\ 12'$; $tg^1 = 120^\circ\ 24'$; $pt = 114^\circ\ 40'$; $pg^1 = 86^\circ\ 10'$.

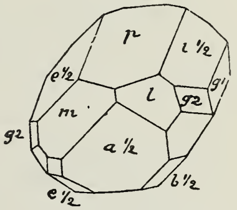
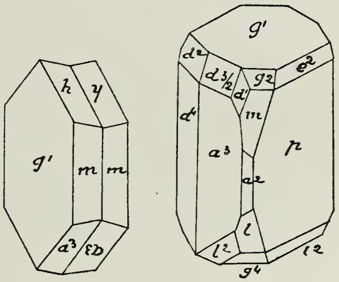


FIG. 26.—Oligoclase.

V. *Albite* ($Si_6O_{16}Al_2Na_2$).—This felspar occurs as milky-white crystals with vitreous lustre, and nearly always macleated. The maclea known as albite exhibits the appearance of a characteristic trough-like depression formed by the juxtaposition of two faces (p) sloping in opposite directions.

Albite frequently occurs as veins in granite, gneiss, diorite, etc. It is unattacked by acids, and fuses to a vesicular glass before the blowpipe, the flame acquiring a yellow tinge. The degree of hardness varies from 6 to 6·5, and the sp. gr. between 2·54 and 2·64. The crystalline form is that of the anorthic prism, $mt = 120^\circ\ 47'$; $pm = 110^\circ\ 50'$; $pt = 114^\circ\ 52'$; $pg^1 = 86^\circ\ 24'$.



FIGS. 27 and 28.—Albite.

VI. *Orthose* ($Si_6O_{16}Al_2K_2$) is frequently met with as simple or macleated crystals in granites and microgranulites. The most general form of maclea is that known as Karlsbad, wherein two crystals are joined along their plane of symmetry, the one crystal being fixed, whilst the second is turned 180° about the vertical edge of the prism.

Orthose is often encountered in flesh-coloured, rose-red, or white laminar or granular masses, and constitutes an essential element of granite, pegmatite, syenite, gneiss, porphyry, etc.

Occasionally crystals of albite are found deposited regularly on those of orthose, or *vice versâ*. The orthose of volcanic rocks is always transparent.

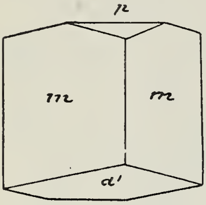


FIG. 29.
Orthose (adular).

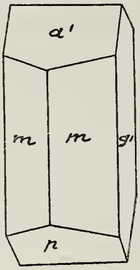


FIG. 30.
Orthose.

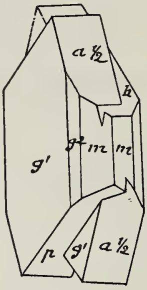


FIG. 31.
Orthose maclea.

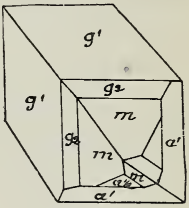


FIG. 32.
Orthose maclea.

In common with other felspars, orthose readily undergoes decomposition, potassium silicate being dissolved out by water, and kaolin left as the final product.

Orthose is unattacked by acids, and is fused, with difficulty, to a vesicular glass. The degree of hardness is 6 to 6·5, and the sp. gr. 2·44 to 2·62. The crystalline form is that of the clino-rhombic prism, $mm = 118^\circ\ 48'$; $pa^1 = 129^\circ\ 40'$.

The felspars are largely utilised in the ceramic industry and for porcelain, and some are employed for the preparation of alum.

CHAPTER II

IRON, AND IRON COMPOUNDS

§ 1. IRON (Fe = 56)

29. **Preparation in the Laboratory.**—The preparation of pure iron in the laboratory will alone be entered into here; the reader desirous of studying the metallurgy of this metal being referred to special works on the subject, wherein a full description is given of the numerous and interesting methods for extracting iron from its ores, and refining and converting the metal into the various products required for use in the industrial arts. In the present work it is sufficient for our purpose to mention that the basis of the metallurgy of iron is the reduction of the various oxide ores, by means of carbon, in special forms of apparatus.

To obtain chemically pure iron in the laboratory, the purest commercial form of iron, namely piano wire, may be treated with ferric oxide and a flux, such as glass, in a refractory crucible exposed to the heat of a blast furnace. In this manner a silver-white bead of metal is obtained.

It is, however, always more convenient to reduce the oxide or chloride of iron by means of hydrogen. By calcining anhydrous ferrous chloride (which can easily be obtained pure) in a current of pure hydrogen, HCl is liberated and pure iron left behind as cubic crystals.

When effected at a high temperature the reduction of ferric oxide in hydrogen yields very finely divided metallic iron. At a lower temperature the product forms a very finely divided mass, shown by Moissan to consist of ferrous oxide. This is the product known by the name of *pyrophoric iron.*

Again, pure iron may be easily prepared by the action of heat on precipitated ferrous oxalate, $C_2O_4Fe = Fe + 2CO_2$.

30. **Properties of Iron.**—*A.* PHYSICAL PROPERTIES.—Iron is bluish grey in colour and of metallic lustre, with a slight metallic odour and taste. It is highly tenacious, an iron wire 1 mm. in diameter requiring a force of 55 kilos to produce rupture. The fracture is granular, and the brilliancy and fineness of grain of the metal are in proportion to its purity. When chilled it becomes brittle, but regains its properties on re-heating. It is malleable and ductile, and may be forged with ease whether cold or hot. The mean sp. gr. is 7·8, but varies according to the method of preparation employed. Thus the sp. gr. of cast iron is 7·5, that of wrought iron being 7·4 to 7·9. The melting point is about 1500°, but before this point is reached the metal becomes soft enough for two surfaces to unite by welding. It is the hardest of the metals in general use, but is marked by glass. Its conductive capacity for heat is represented by 119, compared with silver = 1000; and its electrical conductivity at 20° C. = 14·44, that of silver at 0° being taken as 1000.

Molten iron crystallises in cubes or octahedra, on which account it becomes brittle. Hammering whilst hot prevents it assuming a crystalline structure; nevertheless, it regains this condition by degrees if, after being hammered, it is subjected to repeated vibration.

Iron is magnetic, but loses this property towards 800° C. It is attracted by the magnet, and itself behaves as a magnet so long as contact is maintained, but ceases to act as such when removed. Steel, on the other hand, can be permanently magnetised.

At a red heat iron is permeable by gases, notably by hydrogen, and absorbs them in considerable quantity. It always contains about 12 times its own volume of gas, which it gradually loses when heated in a vacuum. The proportion of gas is much higher in the case of electrolytic iron.

With 2 to 5 per cent. of carbon, iron forms cast iron, melting at about 1250°; but when the proportion of carbon is lower, namely 0·7 to 2 per cent., it becomes steel, the fusing point of which is about 1400° C.

B. CHEMICAL PROPERTIES.—Iron is unalterable in dry air at the ordinary temperature, but at red heat it absorbs oxygen, and is converted into the black, or magnetic, oxide, Fe_3O_4. This combustion goes on very briskly in pure oxygen. In moist air iron undergoes slow oxidation, though only after a considerable time, the metal becoming coated with a layer of hydroxide, known as *rust*. Once formed, this hydroxide constitutes, with the metal, a voltaic couple, in consequence of which the oxidation proceeds more rapidly. In order to protect the metal from this attack it is customary to cover it with a layer of paint, or preferably zinc (galvanised iron), tin (tinned iron), enamel, etc.

At a red heat iron decomposes water, liberating the hydrogen, and itself becoming converted into Fe_3O_4.

Iron unites with a large number of elements. With metals it forms alloys; the metalloids of the chlorine group attack it at the ordinary temperature, and at a high temperature it combines with sulphur, a somewhat fusible sulphide being produced.

Iron decomposes ammonia at red heat, and forms an iron nitride, Fe_5N_2. A large number of dilute acids are also decomposed by iron, with evolution of hydrogen and formation of the corresponding iron salt.

Under the influence of heat, concentrated sulphuric acid is decomposed by iron, sulphur dioxide being liberated. Concentrated fuming nitric acid, however, not only does not attack iron, but also renders the metal proof against the action of weaker acid. In this state the iron is said to have become *passive*. According to some authorities, this condition is attributable to the formation of a stratum of condensed nitrogen dioxide at the surface of the metal as a kind of gaseous sheath. Others, however, regard this explanation as erroneous, and ascribe the passivity of the iron to a deposit of ferro-ferric oxide, which protects the metal from ulterior attack. Nevertheless, this condition of passivity is merely apparent, since in course of time *passive* iron dissolves, without any liberation of gas.

However this may be, if the iron rendered passive by immersion in concentrated acid is afterwards placed in weak acid and touched with a copper wire, the passivity disappears and the metal is attacked energetically.

Very dilute nitric acid dissolves iron without any liberation of gas. In this case the nascent hydrogen produced is converted, by the excess of nitric acid, into ammonia, which remains in solution as ammonium nitrate.

Carbon dioxide in aqueous solution reacts upon iron, forming iron carbonate and hydrogen.

The heat of combination of iron with oxygen, and the halogens, has been determined by Berthelot, who gives the following values:—

Oxygen.	Chlorine.	Bromine.	Iodine.
34,100 cal.	41,100 cal.	35,000 cal.	20,000 cal.

In the case of carbon the combination is endothermic, and the reaction is consequently comparable to solution. With manganese heat is disengaged.

C. ATOMICITY OF IRON.—Iron is capable of entering into combination in several states of basicity, and gives rise to two perfectly distinct series of compounds, corresponding to two different valencies for the metal. In the one set the iron plays the part of a diatomic element, and is represented by the symbol $Fe^{II} = 56$, known by the name of *ferrosum*; whilst in the other case the metal acts as a hexatomic element $(Fe_2)^{VI}$ = *ferricum*.

There is no need to dilate upon the diatomicity of ferrous iron, this condition being sufficiently proved by the existence of ferrous chloride, $Fe^{II}Cl_2$, wherein the metal is combined with 2 atoms of the monovalent element chlorine. To this series of compounds the term *ferrous compounds* is applied.

So far as ferricum, $(Fe_2)^{VI} = 112$, is concerned, this form represents a double atom of iron. It may be asked why the doubling of the iron atom should be regarded as necessary, and whether it would not be simpler to consider ferricum as trivalent $Fe^{III} = 56$. And, in fact, the analysis of ferric chloride gives figures corresponding to $Fe^{III}Cl_3 = 162{\cdot}5$. Nevertheless, an examination of the vapour density of this compound as compared with hydrogen, namely 164·4 (Deville and Troost), leads to the conclusion that the molecular weight is 325, which corresponds to the formula $Fe_2^{VI}Cl_6$, and not $Fe^{III}Cl_3$. In fact, the calculated vapour density works out to 162·5, a value approximating to that determined by Deville and Troost. One is therefore compelled to acknowledge the existence of the double atom of iron, Fe_2^{VI}, constituting a hexatomic couple. Once established, this fact can be explained in other ways. For instance, in iron pyrites or iron disulphide the metal seems to play the part of a tetratomic element. This, however, is merely hypothetical, since the tetravalence of iron could only be established by the existence of a compound of 1 atom of the metal with 4 atoms of a monovalent element. Nevertheless, if we admit this tetravalence, we can equally acknowledge the possibility of one such atom of iron coalescing with a similar one to form the hexavalent group

$$(Fe^{IV}—Fe^{IV})^{VI}.$$

This is equivalent to supposing that the diatomic iron of ferrous chloride, become tetravalent under the influence of an excess of chlorine, exchanges with itself the two valencies corresponding to the 4th atom of chlorine of each of the 2 molecules of the tetrachloride, which is therefore not formed. Ferric chloride is therefore

$$FeCl_3—FeCl_3 = \left.\begin{array}{c} Fe^{IV} \\ | \\ Fe^{IV} \end{array}\right\} Cl_6 = Fe_2Cl_6.$$

§ 2. COMPOUNDS OF IRON

31. **Fluorides of Iron.**—*A.* FERROUS FLUORIDES.—I. *Ferrous Fluoride* (FeF_2).—This salt is prepared by the action of iron on HF, and forms small white crystals, slightly soluble in water, but more freely so in an excess of acid.

In hydrofluoric acid, sp. gr. 1·07, iron dissolves slowly, forming at the end of several days a green solution which, on evaporation, furnishes green prisms, adhering firmly to the walls of the basin and corresponding to the formula

$$FeF_2, 8HO.$$

At a high temperature this salt melts in its own water of crystallisation, and subsequently dries to a white saline mass if air has been excluded during the operation. On exposure to the air, HF is liberated and a mixture of ferric oxide and ferric fluoride is left. On adding nitric acid to a solution of ferrous fluoride a colourless liquid is formed, which, when concentrated, yields a white crystalline mass composed of a mixture of ferric nitrate and ferric fluoride.

II. *Ferro-potassic Fluoride* (K_2FeF_4) is soluble, and crystallises in greenish granular crystals.

III. *Ferrous Fluosilicate* (FeF_2, SiF_4) is prepared by dissolving iron in hydrofluosilicic acid. It is very soluble, and crystallises with difficulty in bluish-green, regular hexagonal prisms.

B. FERRIC FLUORIDES.—I. *Ferric Fluoride* (Fe_2F_6).—To prepare this compound, calcined ferric oxide is treated with an excess of HF. The mixture, which heats spontaneously, is then placed in a large platinum crucible, the lower portion of which is raised to a white heat. The fused mass is of a reddish colour, probably due to contained ferric oxide.

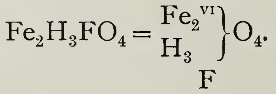
Ferric fluoride is isomorphous with aluminium fluoride, and is just as volatile, though not so fusible, as the latter.

Hydrated ferric fluoride is obtained by oxidising ferrous fluoride with nitric acid in presence of HF, the resulting solution being easy to crystallise. It may also be prepared by dissolving ferric hydrate in hydrofluoric acid.

Ferric fluoride forms colourless or yellowish crystals, only slightly soluble in water, and insoluble in alcohol, their composition being $Fe_2F_6, 9H_2O$. At 100° C. it parts with one-third of its water and becomes $Fe_2F_6, 6H_2O$; and on being dehydrated completely, by the application of greater heat, it liberates hydrofluoric acid concurrently with water.

Ferric fluoride exhibits the remarkable property of not undergoing complete decomposition under the influence of alkalis. Thus an addition of ammonia gives a yellow precipitate, from which caustic potash removes a small quantity of hydrofluoric acid, but not the whole.

This salt exhibits a constant composition, which corresponds to the formula



$$Fe_2H_3FO_4 = \begin{array}{c} \left.\begin{matrix} Fe_2^{VI} \\ H_3 \end{matrix}\right\} O_4. \\ F \end{array}$$

II. *Ferri-potassium Fluorides.*—The salt Fe_2F_6, 6KF is formed in presence of an excess of potassium fluoride, whereas if ferric fluoride be in excess the resulting compound is Fe_2F_6, 4KF. Both these salts, which are crystalline and soluble, were described by Berzelius.

III. *Ferri-sodium Fluoride.*—The formula of this salt is Fe_2F_6, 4NaF + H_2O, and it is prepared by mixing solutions of ferric chloride and sodium fluoride, a precipitate, soluble in an excess of ferric chloride, being formed. On adding alcohol to the solution the salt

$$Fe_2F_6, 4NaF, H_2O$$

is thrown down as yellow flakes.

The iron in this compound cannot be detected by potassium thiocyanate; and moreover, the same reagent, when coloured red by a ferric salt, is decolorised on the addition of an alkali fluoride, in consequence of the formation of a compound of similar type to the above.

IV. *Ferri-ammonium Fluoride* (Fe_2F_6, $6NH_4F$).—This salt was described by Marignac. It is but sparingly soluble in water, and crystallises in small, very lustrous regular octahedra, which do not lose in weight at 100° C.

V. *Ferric Fluosilicate* is obtained by dissolving ferric hydrate in hydrofluosilicic acid.

32. **Chlorides of Iron.**—*A.* FERROUS CHLORIDES.—I. *Ferrous Chloride* ($FeCl_2$).—This is prepared by passing a current of dry hydrochloric acid gas over red-hot iron. Hydrogen is liberated, and crystalline needles of ferrous chloride sublime in the cold parts of the apparatus. Another method is to heat sal ammoniac (ammonium chloride) with iron filings, ferrous chloride being left behind as a residue.

When ferric chloride is carefully heated in a current of hydrogen, well formed crystals of ferrous chloride are obtained.

Ferrous chloride is a white, slightly yellowish salt, volatile, readily soluble in water and also soluble in alcohol.

When heated in a current of hydrogen it furnishes HCl, and cubical crystals of iron are left. In a current of oxygen it forms ferric chloride, chlorine being liberated.

Hydrated ferrous chloride ($FeCl_2, 4H_2O$) is prepared by dissolving the anhydrous chloride in water, or by acting on iron with hydrochloric acid. By this means a green solution is obtained which, on concentration, furnishes the hydrated chloride in the form of bulky green crystals, derived from the clinorhombic prism.

Ferrous chloride is less soluble in HCl than in water, so that, when a current of HCl gas is passed through the aqueous solution of this salt, crystals are deposited. If anhydrous ferrous chloride be dissolved in hot concentrated hydrochloric acid, and the solution left to crystallise, fine transparent needles corresponding to the formula $FeCl_2, 2H_2O$ are obtained.

When strongly heated, $FeCl_2, 4H_2O$ melts in its water of crystallisation, and, if the heating be continued, gradually loses its moisture, a white residue being finally left, provided air has been excluded during the operation. In contact with air, however, ferric chloride is formed, which is carried away by the liberated water vapour, and leaves behind a green fusible mass. This yields up ferrous chloride to water, and a residue of ferrous oxide, rapidly oxidising in the air, is left.

Ferrous chloride solution absorbs nitrogen dioxide to a much greater extent than the dry salt; and the alcoholic solution absorbs a still larger quantity of this oxide.

Gaseous ammonia reacts at a red heat on ferrous chloride, with formation of ferric nitride, Fe_5N_2. In the cold, ferrous chloride absorbs NH_3 and forms $FeCl_2, 6NH_3$. Ferrous chloride is insoluble in ether.

II. *Ferro-potassium Chloride* ($FeCl_2, 2KCl$).—Ferrous chloride and potassium chloride readily crystallise together, to furnish the compound $FeCl_2, 2KCl$, when a mixture containing in solution suitable proportions of these two salts is left to cool.

III. *Ferro-ammonium Chloride* resembles the foregoing salt, and is prepared in the same manner.

IV. *Intermediate Ferrous Chloride.*—Hensgen prepared the chloride $Fe_3Cl_4, 5H_2O$, in fine pale green needles, by dissolving ferrous sulphate in HCl, and saturating the mixture with gaseous hydrochloric acid in contact with air.

V. *Ferro-ferric Chloride.*—According to Lefort, the compound Fe_3Cl_4, $18H_2O$ is obtained when a solution of ferro-ferric oxide in HCl is evaporated over H_2SO_4 and CaO, the latter substance being employed to absorb the excess of HCl.

B. FERRIC CHLORIDE.—I. *Anhydrous Ferric Chloride* ($Fe_2Cl_6 = 325$).—This salt is prepared by passing a current of dry chlorine over red-hot iron. We have seen that, to obtain ferrous chloride, iron is treated with HCl; and these two methods are general. When any metal forms two compounds with chlorine, the one containing the smaller proportion of that element is obtained by the action of HCl, the richer by the action of chlorine.

When sublimed, ferric chloride assumes the form of tabular hexagonal crystals, dark red in colour with a greenish reflection.

The vapour density of this body is 162·5, Deville and Troost having found the value 164·4 compared with H = 1.

Ferric chloride is soluble in water, with evolution of heat, different hydrates being formed. Franz has compiled the following table, showing the density of the aqueous solutions of this salt at 17·5° C.:—

Density.	Fe_2Cl_6.	Density.	Fe_2Cl_6.
1·0146	2 per cent.	1·2778	32 per cent.
1·0292	4 ,,	1·2988	34 ,,
1·0439	6 ,,	1·3199	36 ,,
1·0587	8 ,,	1·3411	38 ,,
1·0734	10 ,,	1·3622	40 ,,
1·0894	12 ,,	1·3870	42 ,,
1·1054	14 ,,	1·4118	44 ,,
1·1215	16 ,,	1·4367	46 ,,
1·1378	18 ,,	1·4617	48 ,,
1·1542	20 ,,	1·4867	50 ,,
1·1746	22 ,,	1·5153	52 ,,
1·1950	24 ,,	1·5439	54 ,,
1·2155	26 ,,	1·5729	56 ,,
1·2365	28 ,,	1·6023	58 ,,
1·2568	30 ,,	1·6317	60 ,,

It is also soluble in alcohol and ether, but the solutions are unstable, and on exposure to light liberate chlorine (which reacts on the solvent) and furnish ferrous chloride.

At a red heat, ferric chloride is decomposed by steam, hydrochloric acid and ferric oxide being formed. This reaction, which can also be effected in a closed vessel, was utilised by Sénarmont for the production of crystalline ferric oxide. When treated in oxygen it is converted into ferric oxide, chlorine being liberated.

Anhydrous ferric chloride readily combines with a number of different substances. With ammonia it forms a red mass, $Fe_2Cl_6, 2NH_3$, soluble in water and easily decomposed by heat. With phosphorus pentachloride it gives a brown, fusible mass, corresponding to the formula $Fe_2Cl_6, 2PCl_5$; and with nitroxyl chloride yields a dark, deliquescent mass, $Fe_2Cl_6, 2NOCl$.

II. *Hydrated Ferric Chloride* may be prepared by the action of water on the anhydrous chloride; or by treating a solution of ferrous chloride with chlorine; or again, by acting on ferrous chloride with nitric acid or nitrohydrochloric acid.

When ferric hydrate is acted on by HCl, a solution of ferric chloride containing an excess of dissolved ferric hydrate is obtained.

On concentration, the solution of ferric chloride deposits rhombohedral plates of a handsome yellow colour, containing 6 or 4 molecules of water: $Fe_2Cl_6, 6H_2O$ or $Fe_2Cl_6, 4H_2O$. The first of these salts melts at 31°, and the second at 35·5° C. On slowly evaporating a dilute solution of ferric chloride, the first crystals formed respond to the formula $Fe_2Cl_6, 12H_2O$.

According to A. Vogel, dissolved ferric chloride is to a small extent volatilised below boiling point. With ether this volatilisation takes place at about 30° C.

On heating a solution of this salt, diluted to such an extent as to be almost colourless, it assumes a deep coloration beyond 27° C., without parting with hydrochloric acid. Its properties, however, will be found to have undergone considerable modification, the precipitate formed with potassium ferrocyanide being now only of a pale bluish-white shade, whilst saline solutions throw down a precipitate of modified ferric hydrate. When dialysed, the solution divides into soluble hydrate and hydrochloric acid.

If, after the modified ferric hydrate has been precipitated by sodium chloride, it is left at rest for 24 hours before filtering, it will no longer dissolve in water.

Under the influence of heat the solution is split up into free hydrochloric acid and the "colloid hydrate" of Graham.

The more dilute the solution of ferric chloride, the more readily is it dissociated under the influence of heat; the products vary according to the temperature, duration of heating, and concentration of the solution under examination. Thus a 40 per cent. solution is not decomposed below 100° C. A 32 per cent. solution furnishes a yellow oxychloride at 120° C., and brown ferric oxide at 140° C. An 80 per cent. solution yields an oxychloride of variable composition at 110° C.; whilst a 40 per cent. solution gradually deepens in colour up to 90° C., and then furnishes an oxychloride. Before precipitation occurs these solutions contain Graham's "colloid hydrate," which can be separated by means of NaCl.

If the heat has not been too great or too prolonged, the solutions containing between 4 and 32 per cent. of ferric chloride will regain their original condition on cooling. This reversion is more gradual in the case of 1 to 4 per cent. solutions, and incomplete in solutions below 1 per cent. strength.

Solutions containing $\frac{1}{16}$ per cent. of Fe_2Cl_6 decompose when exposed to light, even at 5° or 6° C., but $\frac{1}{8}$ per cent. solutions are stable under the same conditions at the ordinary temperature. The decomposition of these solutions is attended by an alteration, though slight, in their specific gravity.

When a solution of Fe_2Cl_6 is heated for some time at 100° C. the soluble hydrated oxide is converted into a form insoluble in weak acids, but dissolving in water to a solution which is transparent by transmitted light, but turbid when viewed by reflected light. Heated to 250° to 300° under pressure, the anhydrous oxide is formed.

In solution in alcohol, even when diluted, Fe_2Cl_6 does not undergo any appreciable dissociation.

When an acid solution of this salt is subjected to electrolysis, ferrous chloride is obtained at the negative pole, whilst chlorine collects at the positive pole.

On treating pure neutral Fe_2Cl_6 with sodium sulphite solution in equal molecular proportions, a very intense, but transitory, blood-red coloration is immediately produced, which is attributed by Buignet to the formation of a sulphite of ferric oxide.

Ferric chloride is reduced by most reducing agents: nascent hydrogen, metals, etc. Even platinum is somewhat readily attacked by Fe_2Cl_6, probably by the chlorine, which, according to Personne, is always liberated when a sufficiently strong solution of this salt is heated to boiling.

Sulphuretted hydrogen, sulphur dioxide, and stannous chloride also reduce Fe_2Cl_6.

On agitating a solution of this salt with ether, the latter assumes a yellow colour and extracts the Fe_2Cl_6 from the water.

Ferric chloride is largely used as a hæmostatic, and may be administered internally without risk. It has been recommended in the treatment of croup, and is used for purifying waste waters.

III. *Compounds with other Chlorides.*—According to Hensgen, the salt $Fe_2Cl_6, 2NH_4Cl, 2H_2O$ is formed when ferro-ammonium sulphate is treated with HCl in contact with air.

Fe_2Cl_6 forms with $PtCl_4$ a compound ($Fe_2Cl_6, 2PtCl_4, 24H_2O$) which crystallises in deliquescent clinorhombic prisms, and parts with $10H_2O$ at 100° C.

IV. *Oxychlorides of Iron.*—These compounds are numerous, and are divided into 2 series, namely soluble and insoluble oxychlorides, corresponding respectively to compounds of the soluble or insoluble hydrate with Fe_2Cl_6.

When left for some time, solutions of ferric chloride gradually deposit a yellow-brown powder, $Fe_2Cl_6, 6Fe_2O_3, 9H_2O$, which on gentle calcination in air is converted into $Fe_2Cl_6, 3Fe_2O_3, H_2O$.

If a concentrated solution of ferrous chloride be oxidised by means of the theoretical quantity of nitric acid in presence of an insufficiency of HCl, the solution being heated to 100° C. and the nitric acid added by degrees, a very brisk reaction is set up; the liquid, which was initially black, becomes yellow and turbid, and yields on filtration a yellow precipitate remarkable for the tenacity with which it retains chlorine. This precipitate is insoluble in water, sparingly soluble in HCl, and varies in composition according to the proportions of ingredients taken. When the amount of HCl employed is about one-third of that theoretically necessary to form Fe_2Cl_6, the precipitate consists of

$$Fe_2Cl_6, 12Fe_2O_3,$$

and on digestion with water is transformed into the still more basic oxychloride

$$Fe_2Cl_6, 17Fe_2O_3.$$

When digested for 24 hours with ammonia the composition becomes

$$Fe_2Cl_6, 144Fe_2O_3,$$

and after boiling with NH_3 still retains 0·85 per cent. of Fe_2Cl_6.

The majority of the oxychlorides are prepared by dissolving freshly precipitated ferric hydrate in a solution of Fe_2Cl_6. At first, solution goes on rapidly, but when a certain point is reached the operation slackens and the liquid sets to a dark coloured jelly, which is soluble in water and contains

$$Fe_2Cl_6, 12Fe_2O_3.$$

By the addition of water a further quantity of hydrate can be brought into solution, the liquid then containing $Fe_2Cl_6, 20Fe_2O_3$ according to Béchamp, or even $Fe_2Cl_6, 23H_2O$ according to Ordway.

The oxychlorides $Fe_2Cl_6, 5Fe_2O_3$ to $Fe_2Cl_6, 10H_2O$ may be dried without losing their solubility, whereas the others are thereby rendered insoluble. These solutions exhibit an acid reaction, and are precipitable by the addition of a salt or HCl. They are also precipitated by NH_3, and then furnish ferric hydrate free from chlorine, whereas the insoluble oxychlorides, even when boiled for a long time with NH_3, always retain a little chlorine. This fact is ascribed by Béchamp to a difference of molecular condition.

By digesting freshly precipitated chromium hydrate with a solution of Fe_2Cl_6 for several months, Béchamp obtained a soluble compound of ferric chloride and chromium oxide, $Fe_2Cl_6, 4Cr_2O_3$.

The oxychlorides of iron have been principally investigated by Béchamp and Ordway.

33. **Chlorates of Iron.**—*A.* FERROUS CHLORATE $(ClO_3)_2Fe$.—This salt is prepared from barium chlorate and ferrous sulphate

by double decomposition. Its solution is split up, by boiling, into chlorine and ferric chlorate.

B. FERRIC CHLORATE $(ClO_3)_6Fe_2^{VI}$.—In addition to the preceding reaction, this salt may also be formed by the action of chlorine on ferrous hydrate suspended in water, a yellowish-red liquid being thereby obtained.

C. FERROUS PERCHLORATE, $(ClO_4)_2Fe$, may be prepared by dissolving iron in perchloric acid, or by double decomposition. It crystallises in small greenish, deliquescent crystals containing $6H_2O$. The solution oxidises on exposure to air, and deposits a basic ferric perchlorate. It decomposes above 100° C.

D. FERRIC PERCHLORATE $(ClO_4)_6Fe_2^{VI}$.—This has only been obtained in a state of solution.

34. **Bromides of Iron.**—*A.* FERROUS BROMIDE ($FeBr_2$) is obtained by treating an excess of iron with bromine. In the anhydrous condition it forms a light yellow, fusible, lamellar mass dissolving in water to a greenish solution, from which crystals of $FeBr_2$ are deposited on concentration. Under the influence of air this solution throws down an insoluble yellow oxybromide.

B. FERRIC BROMIDES.—I. *Ferric Bromide* (Fe_2Br_6).—This salt is obtained in solution when iron is treated with an excess of bromide; and in the anhydrous condition by treating hot iron with bromine vapour, the ferric bromide subliming in the latter case as dark red scales.

II. *Oxybromides* are formed under the same conditions as the oxychlorides.

Béchamp obtained $Fe_2Br_6, 14Fe_2O_3$ by dissolving ferric hydrate in a solution of ferric bromide.

Like the oxychlorides, the solutions of the oxybromides are deep red, and possess considerable tinctorial power.

35. **Bromates of Iron.**—*A.* FERROUS BROMATE (BrO_3Fe).—To prepare this salt, ferrous carbonate is dissolved in bromic acid, the bromate crystallising in regular octahedra when the solution is evaporated *in vacuo.* It is of low stability, and continually manifests a tendency to decompose, with formation of a ferric sub-salt.

B. FERRIC BROMATE $(BrO_3)_6Fe_2^{VI}$. — Freshly precipitated ferric hydrate will dissolve in dilute bromic acid to form ferric bromate. The solution refuses to crystallise, and readily decomposes with formation of a basic salt.

36. **Iodides of Iron.**—*A.* FERROUS IODIDE (FeI_2).—When a mixture of iron filings and iodine is rapidly heated to redness, and a further addition of iodine made on the attainment of that temperature, a fused mass containing periodide is obtained, which suddenly liberates iodine at a particular stage of cooling, and leaves a grey lamellar mass of ferrous iodide.

Another method of preparation is by gradually adding iodine to iron filings under water, a paler green, readily oxidisable solution being obtained, which can only be concentrated in a current of hydrogen. Under these conditions a deposit of $FeI_2, 4H_2O$ (sp. gr. = 2·873) is formed. In a pure anhydrous state this salt is white and pulverulent. When heated in the air it loses iodine and leaves a magnetic residue; on exposure to moist air it turns greenish, and assumes a crystalline texture.

B. FERRIC IODIDE (Fe_2I_6) is prepared by treating ferric hydrate with hydriodic acid, or by acting on iron with an excess of iodine. It forms a brown, uncrystallisable solution.

37. **Iodates of Iron.**—*A.* FERROUS IODATE, $(IO_3)_2Fe$, is a slightly soluble light red precipitate, obtained by double decomposition.

B. FERRIC IODATE $(IO_3)_6Fe_2^{VI}$.—Obtained in the form of a yellow precipitate by heating a mixture of ferrous chloride and an alkali iodide in presence of an excess of nitric acid.

C. FERRIC PERIODATE ($I_2O_{13}Fe_2, 21 H_2O$).—This salt may be obtained, as a brown-yellow precipitate, from periodic acid and ferric hydrate; but not by double decomposition, because in the latter event it is transformed into the iodate.

38. **Oxides of Iron.**—*A.* IRON SUB-OXIDE.—According to Marchand, this is the product formed when iron wire is fused in the oxyhydrogen blowpipe flame. It is a fusible, malleable, black oxide, soluble with some difficulty in HCl and H_2SO_4. Marchand found it to contain a constant proportion of 6·79 per cent. of oxygen. According to Dusart, a sub-oxide of iron is also formed when ferric oxide is reduced by hydrogen; but Moissan, who

has carefully investigated this reduction, is unable to confirm the alleged result.

B. Ferrous Oxide.—I. *Anhydrous Ferrous Oxide* (FeO).—This oxide was prepared by Debray by passing a mixture of equal volumes of carbon monoxide and carbon dioxide over red-hot ferric oxide.

It is also obtained as a crystalline, black, lustrous, magnetic substance when carbon dioxide is reduced by means of metallic iron. On calcination in air, or in a current of steam, this anhydrous oxide is converted into magnetic oxide, Fe_3O_4.

A pyrophoric ferrous oxide capable of decomposing water is obtained by heating the oxalate to 500° C. in a current of hydrogen. At 350° C. ferro-ferric oxide is produced, and metallic iron at between 500° and 700° C.

II. *Ferrous Hydrate.*—When a ferrous salt is precipitated by a base, white flakes of ferrous hydrate are formed. This compound is very unstable in air, and cannot be washed and dried without undergoing alteration.

Ferrous hydrate is slightly soluble in water, the solution exhibiting a pronounced ferruginous taste, an alkaline reaction, and a tendency to soon become turbid on exposure to the air. When treated with KHO at boiling temperature this hydrate turns black, the magnetic oxide being formed, and hydrogen liberated.

C. Ferro-ferric Oxide, or Magnetic Oxide of Iron.—I. *Anhydrous Ferro-ferric Oxide* ($Fe_2O_3, FeO = Fe_2^{VI}Fe''O_4 = Fe_3O_4$).—The crude formula employed for this oxide is Fe_3O_4, but it may be regarded as a combination of ferric oxide with ferrous oxide, *i.e.* as a ferrite of ferrous oxide. Again, it may be considered as an intermediate oxide between FeO and Fe_2O_3, and for this reason will not be described among the ferrites.

Fe_3O_4 is found in terrestrial rocks, either in the amorphous state or crystallised in octahedra, and occurs in meteorites. It forms the best iron ore, is characterised by its magnetic properties, and constitutes the natural loadstone met with very abundantly in Sweden and Norway, where it occurs in compact masses endowed with a metallic lustre, and of sp. gr. 5·09.

This oxide may be produced under various conditions, *e.g.*, by the combustion of iron in an excess of oxygen; or, as a dense black powder, by fusing ferrous chloride with dry sodium carbonate at a low temperature. It is also obtained by roasting iron in the air, by the action of boiling water on ferrous hydrate, by the action of iron filings on ferric hydrate in boiling water. In both the last-named cases hydrogen is liberated.

According to Deville, ferro-ferric oxide is obtained as octahedral crystals mixed with chloride, when a current of HCl is passed slowly over ferrous oxide. It has also been prepared by Sidot, as octahedral crystals, by heating colcothar to a very high temperature for 2 hours.

Moissan has prepared two allotropic modifications of this oxide: the one by heating ferric oxide to about 350° to 400° C. in a current of hydrogen or carbon monoxide, or by heating ferro-ferric hydrate or ferrous carbonate to about 300° C.; the second modification being obtained by reactions carried on at a high temperature, such as the combustion of iron in oxygen.

The first-named type is black, highly magnetic, susceptible to the action of HNO_3, and exhibits a sp. gr. = 4·86, whilst the other, though black and magnetic, is impervious to this acid, and is of higher density, namely 5 to 5·10.

II. *Ferro-ferric Hydrate* is prepared by precipitating an equimolecular solution of ferrous sulphate and ferric sulphate by NH_3. The solution is poured into the reagent, since, if the converse method be adopted, a mixture (but not the compound) of ferrous hydrate and ferric hydrate will be thrown down. Ferro-ferric hydrate is of a dark green colour, and yields a black powder on desiccation.

III. *Intermediate Oxides.*—These comprise a number of oxides richer in FeO than the magnetic oxide, and formed when iron is heated to redness in presence of air.

Authorities are not agreed as to the composition of the members of this series. Berthier obtained $Fe_2O_3, 4FeO$, and Mosander $6FeO, Fe_2O_3$; and, according to the latter, the various figures given by different authors are due to the formation of successive layers of oxides, of different constitution, on the surface of iron heated to redness in the air. These oxides, however, cannot be regarded as definite chemical entities.

IV. *Oxide* (Fe_2O_3, $9FeO$).—This product was found by O. Veelker on a natural magnetic oxide from Prévali in Carinthia.

D. FERRIC OXIDE.—I. *Anhydrous Ferric Oxide*, (syn.: Sesquioxide, or peroxide, of iron) (Fe_2O_3).—When iron, or its magnetic oxide, is calcined for a considerable time in the air, Fe_2O_3 is produced. A simpler method, however, is to calcine the ferric hydrate obtained on precipitating a ferric salt by an alkali. It is also readily obtained by calcining nitrates or sulphates of iron; and this last-named process is adopted on an industrial scale for the manufacture of Nordhausen sulphuric acid and *colcothar*, or commercial ferric oxide,

$$(SO_4)_3Fe_2 = Fe_2O_3 + 3SO_3,$$
$$2SO_4Fe = SO_3 + SO_2 + Fe_2O_3.$$

If the iron sulphate be mixed with common salt, the Fe_2O_3 formed on calcination is in the condition of nearly black crystalline fibres.

Iron sulphide also furnishes Fe_2O_3 when calcined.

Crystallised ferric oxide may be obtained by decomposing ferric chloride by means of lime at red heat (Daubrée). When ferric oxide is fused with borax before the blowpipe flame, and the resulting greyish-green mass is dissolved in hot nitric acid, Fe_2O_3 is left in the condition of orange-coloured rhomboidal prisms with 5 or 6 facets.

In colour ferric oxide is a more or less dark red, sometimes nearly black, hygroscopic, and very hard. It is employed for polishing metals, glass, etc. On prolonged exposure to white heat it is converted into Fe_2O_3, FeO. It is not magnetic, though, according to Malaguti, a magnetic anhydrous ferric oxide does exist.

Ferric oxide is obtained by calcining organic ferrous salts in air, ferrous carbonate oxidised spontaneously by exposure to air, etc. Magnetic ferric oxide is produced by deflagrating ferroferric oxide with $KClO_3$.

When heated towards 300° C., ferric oxide resembles finely divided amorphous phosphorus in colour; whilst under the same conditions magnetic ferric oxide is a light brick-red. This latter oxide also differs from the ordinary form in point of density and specific heat: thus ordinary ferric oxide has an average sp. gr. of 4·784 at 15° C., whereas that of the magnetic form is 4·686. In both cases the density is increased to 5·144 by strong calcination, but the magnetic oxide is thereby rendered inert. The specific heat of the non-magnetic oxide is 0·1794; that of the magnetic oxide is 0·1863; and by strong calcination (destroying the magnetic property of the latter oxide) these values are modified to 0·1730–0·1734.

The oxide obtained from meteoric iron is also magnetic, a property shown by Smith to be attributable to the presence of a small quantity of nickel and cobalt.

On exposure to red heat, ordinary ferric oxide undergoes incandescence and becomes of a brighter red colour, harder, and more difficult to dissolve in acids. It is insoluble in HNO_3, the best solvent being a mixture of 8 parts of H_2SO_4 and 3 parts of water. The specific heat of the oxide is lowered by calcination.

Ferric oxide is reduced by carbon, hydrogen, etc., and is converted by SO_2 into ferrous oxide, which unites with the sulphuric acid formed. It is attacked by phosphorus pentachloride; and ammonia reduces it to the state of metallic iron containing nitrogen. On the other hand, it is not reduced by stannous chloride, even at boiling heat.

Ferric oxide is an energetic oxidising agent, and its power is, so to speak, illimitable, because of its recuperative capacity in contact with air, after parting with oxygen to oxidisable substances, the Fe_2O_3 thus reconstituted being again in a position to give up a further quantity of oxygen.

It is on this account that, in course of time, nails embedded in wood damage the portions in their immediate vicinity; and fabrics spotted with rust quickly fall in holes.

P. Thénard ascribes an important rôle in nature to ferric oxide, and considers that it oxidises organic matter, the nitrogen of which it converts into nitrates.

Ferric oxide is very extensively found in nature, and constitutes the most abundant ore of iron. For industrial purposes it is used, under the name of *colcothar*, as a polishing material for metals and glass; as a pigment; for decolorising syrups in the sugar refinery, and it also enters into the composition of enamels and glazes in the ceramic industry.

II. *Ferric Hydrates*.—Several of these are known, but their investigation is a somewhat difficult matter, and their exact formula hard to define.

An examination of the various natural ferric hydrates may serve as a starting-point or basis for the study of these products.

Turgite, or *Hydrohaematite*, consists of $2Fe_2O_3, H_2O$; *gœthite* is Fe_2O_3, H_2O; *limonite*, $2Fe_2O_3, 3H_2O$; and the brown mineral of Huttenrode (Murray), $Fe_2O_3, 2H_2O$.

If a dilute solution of ferric chloride be precipitated by NH_3, and the precipitate dried over sulphuric acid after washing with alcohol and ether in succession, the mass will exhibit at the end of 2 months' storage the same composition as Huttenrode ore, namely $Fe_2O_3, 2H_2O$.

The precipitate obtained by treating ferric chloride with an alkali is probably the hydrate $Fe_2O_3, 3H_2O$. This compound dissolves readily in acetic acid, and the resulting solution gives a precipitate of Prussian blue with potassium ferrocyanide. It readily parts with water. When dried *in vacuo* it becomes $2Fe_2O_3, 3H_2O$, and therefore corresponds to limonite. Heated to 100° under water for several minutes it again undergoes dehydration and then becomes Fe_2O_3, H_2O, analogous to gœthite. If the boiling be prolonged, more and more of the water of hydration is set free, and the whole is lost on heating in a sealed tube to a temperature approaching 160° C. (de Sénarmont).

Another method of preparing the hydrate Fe_2O_3, H_2O is by precipitating a boiling solution of ferrous carbonate by a mixture of sodium carbonate and sodium hypochlorite. In the cold the reaction is more protracted, and the precipitate contains $Fe_2O_3, 2H_2O$.

A compound, with the formula $3Fe_2O_3, 5H_2O$, is obtained by adding basic ferric sulphate to caustic potash in a state of fusion. H. Brunck and C. Graebe found Fe_2O_3, H_2O in the product of the action of caustic soda on a cast-iron boiler. This substance occurred as a friable mass composed of lustrous lamellæ, of sp. gr. 2·91, unaffected by cold H_2SO_4 or HNO_3, and but slowly soluble in cold HCl.

These various hydrates are of different shades of colour, ranging from yellow to dark brown. D. Tommasi classifies them, according to the ease with which they give up their water, into

(1) *The brown hydrates obtained on precipitating ferric salts by an alkali.*

(2) *The yellow hydrates resulting from the oxidation of ferrous or ferro-ferric hydrates, and of ferrous carbonate.*

Those of the first class are more easily dehydrated than the others, and furnish a brown anhydrous oxide, of sp. gr. 5·11, readily soluble in acids. The oxide from those of the second class is red, of sp. gr. 3·95, and only sparingly soluble in acids.

On gently heating the hydrate obtained by precipitating ferric chloride by ammonia, so as to drive off all the water, and then applying stronger heat, the mass suddenly becomes incandescent, without alteration of weight, and leaves an anhydrous oxide more indifferent than if prepared at a lower temperature.

If ordinary ferric hydrate be heated to 100° C. for 7 or 8 hours, it acquires properties differing from those it originally possessed. At the end of several minutes the composition has altered and become Fe_2O_3, H_2O, as we have already seen. The colour, too, has changed from ochre-yellow to brick-red; and boiling concentrated nitric acid only dissolves it by degrees, nor is it dissolved by HCl, except by boiling or prolonged digestion. No longer does it give a precipitate of Prussian blue with acetic acid and potassium ferrocyanide; and when heated to redness it no longer becomes incandescent, but behaves as though already calcined.

When dried, this modified hydrate is pulverulent, whereas the ordinary hydrate yields hard, brittle fragments.

The following facts, investigated by Péan de St. Gilles, Scheurer-Kestner, and Graham, also tend to prove the existence of a modified form of ordinary ferric hydrate.

If ferric acetate be prepared in the cold, from the precipitated hydrate and acetic acid, a more or less reddish liquid, presenting all the characteristic of the ferric salts, is obtained. On boiling this liquid the colour suddenly becomes 4 or 5 times more intense, and concurrently a powerful odour of acetic acid is noticeable, without any precipitation occurring. If the heating be carried on in sealed tubes at about 100° C., on the water bath, the liquid will be found progressively modified, at the end of several hours, the colour becoming a lighter red without any alteration in intensity. Viewed by reflected light it appears turbid, but is still perfectly limpid and homogeneous by transmitted light; it has, however, entirely lost the usual taste of iron salts, and now exhibits only that of acetic acid; a Prussian blue precipitate is no longer formed with potassium ferrocyanide, and no increase in the depth of colour is produced by potassium thiocyanate. On the other hand, the addition of a trace of H_2S or of an alkali salt precipitates the whole of the ferric hydrate present, in the form of a red deposit insoluble in acids; and this hydrate, when dried on a sheet of glass, forms small blackish-brown lustrous plates, soluble in pure water, and furnishing a liquid which is turbid by reflected light but transparent by transmitted light, highly coloured and devoid of any appreciable flavour. This liquid may be precipitated anew by concentrated HCl, HNO_2, etc.

The same result is obtained from ferric nitrate; and in the case of this salt Scheurer-Kestner observed that light produces the same effects as heat.

These phenomena are evidently of the same order as those occurring when solutions of ferric chloride are exposed to the influence of heat.

The resulting liquids can no longer be regarded as solutions of ferric salts—acetates, nitrates, chlorides, etc.; but one is compelled to look upon them as acid solutions of modified ferric hydrate, or as emulsions of this hydrate in dilute acids, the latter acting mechanically and separating the particles of hydrate into an extremely fine state of division.

On saturating ferric chloride with ferric hydrate and dialysing the resulting red liquid, the latter parts with almost the whole of its acid and leaves behind in the dialyser a deep blood-red liquid, highly charged with ferric hydrate, which can be concentrated, to a certain degree, by boiling without becoming coagulated.

This solution may be coagulated in the cold by adding a trace of H_2SO_4, by an alkali, and by a large number of salts; but no turbidity is produced by HNO_3, HCl, or alcohol.

The coagulum forms a dark red jelly, which though insoluble in water is readily dissolved by dilute acids. It constitutes the "colloid hydrate" of Graham.

When the liquid obtained by dialysis is evaporated *in vacuo* it leaves the hydrate $2Fe_2O_3, 3H_2O$ (Magnier de la Source), whilst the modified hydrate seems to always contain Fe_2O_3, H_2O.

Freshly precipitated ferric hydrate is employed as an antidote to arsenious acid.

39. **Ferrites.**—This name is applied to compounds of ferric oxide with various protoxides, the ferro-ferric oxide already described being a typical example. Most of these compounds are magnetic.

A. POTASSIUM FERRITE.—Frémy prepared this body by heating to redness a mixture of 1 part of iron with 2 parts of potassium nitrate, and Mitscherlich obtained it by calcining ferri-potassium oxalate. It is yellowish green, and is decomposed by water, which extracts the alkali.

B. SODIUM FERRITE is prepared by the same reactions as the potassium compound, and possesses the same properties.

C. CALCIUM FERRITE, $Fe_2O_3 (CaO)_4$.—This has been obtained by the precipitation of a mixture of 1 molecule of Fe_2Cl_6 and 4 molecules of $CaCl_2$ by caustic potash. The precipitate, yellow at first, gradually becomes white if carefully preserved from contact with air; otherwise it is decomposed by atmospheric carbon dioxide. When boiled it turns white immediately. This ferrite is a light, perfectly white powder, insoluble, decomposed by weak acids (even by CO_2). Neither water nor sugar solution is able to extract the lime.

List obtained the compound CaO, Fe_2O_3 on precipitating a neutral solution of Fe_2Cl_6 by lime water, and drying and calcining the resulting deposit. This product is brown, friable, and magnetic.

J. Percy has prepared a calcium ferrite in voluminous crystals of metallic lustre, and with a sp. gr. = 4·693, by heating to whiteness, and afterwards slowly cooling, a mixture of ferric oxide and lime.

D. BARIUM FERRITE.—A brown, friable, magnetic body, of the formula BaO, Fe_2O_3, was obtained by List by the same method as for calcium ferrite.

E. MAGNESIUM FERRITE is obtained in a similar way from milk of (calcined) magnesia, and forms a brown precipitate, which on calcination agglomerates in highly magnetic, fritted, cannel-brown fragments. When dried over H_2SO_4 this precipitate corresponds to the formula Fe_2O_3, $4H_2O$.

F. ZINC FERRITE.—According to Ebelmen, the compound ZnO, Fe_2O_3 is obtained by heating to whiteness, for several days, a mixture of

1 part ferric oxide,
2 parts zinc oxide,
2 parts boric acid.

When treated with cold dilute HCl the mass parts with zinc borate, and there remains a black powder crystallised in regular octahedra and composed of zinc ferrite, which is soluble in boiling, concentrated HCl.

G. MANGANESE FERRITE. — This is a brown-black precipitate obtained by treating with caustic potash a mixture of equal molecular proportions of manganese and ferric chloride.

H. COPPER FERRITE (CuO, Fe_2O_3, $5H_2O$) is prepared in the same manner, and forms a dirty yellow, voluminous precipitate, which turns blackish brown on calcination.

40. **Ferric Acid.**—Ferric anhydride, discovered by Frémy, has the composition FeO_3; but neither this body nor its hydrate, ferric acid, FeO_4H_2, is known in a free state, though some of its salts have been prepared, among them being K_2FeO_4, which is analogous to K_2MnO_4.

When attempts are made to set ferric acid at liberty it decomposes as follows :—

$$4H_2FeO_4 = 2Fe_2O_3 + 4H_2O + 3O_2.$$

De Mollins confirmed the accuracy of the formula FeO_3 by the analytical results obtained with barium ferrate, namely, from the quantity of iodine liberated by that salt from potassium iodide, according to the equation

$$2FeO_4Ba + 8KI + 16HCl$$
$$= 2BaCl_2 + 8KCl + 2FeCl_2 + 8H_2O + 4I_2$$

41. **Ferrates.**—*A.* POTASSIUM FERRATE (FeO_4K_2).—There are several methods of preparing this salt:—

(1) *Dry Method.*—Five grams of pure iron filings are placed in a Hessian crucible embedded in live coals, and when the metal is red-hot an addition is made of 10 grams of powdered saltpetre, previously freed from moisture by fusing. A brisk reaction immediately ensues, and, after leaving the covered crucible to cool down, a violet-red mass, very rich in potassium ferrate, is obtained.

The same product may also be prepared by the action of saltpetre on iron oxide.

(2) *Wet Method.*—A current of chlorine is passed through a solution of 30 parts of caustic potash in 50 parts of water, in presence of 1 part of freshly precipitated ferric hydrate. An excess of potash is maintained throughout the reaction by suitable additions of this reagent. Finally, a black powder (potassium ferrate) is obtained, which is insoluble in potash but should dissolve completely in water to form a rose-coloured solution.

Potassium ferrate may also be formed under various other conditions: for example, when potassium peroxide is treated with ferric oxide; by the action of an electric current on a solution of caustic potash contained in a cast-iron vessel (Poggendorf); by saturating caustic potash solution with iodine and calcining the saline residue in an iron crucible; etc.

Potassium ferrate is fairly stable when in the solid form or in concentrated solutions, but decomposes very quickly when diluted with water, oxygen being liberated and Fe_2O_3 deposited. The concentrated solution will stand boiling, especially when it contains a mineral salt; the addition of an acid, however, produces immediate decomposition, and ammoniacal salts or reducing agents convert the ferric acid into ferric hydrate.

Potassium ferrate is exceedingly soluble in water, the solution exhibiting a handsome red or violet-red coloration.

B. SODIUM FERRATE is easily prepared by the wet method, by passing a current of chlorine through a concentrated solution of caustic soda containing ferric hydrate in suspension. It is soluble in water.

C. AMMONIUM FERRATE does not appear to exist, since the ferrates are immediately decomposed by NH_3, nitrogen being liberated and a precipitate of Fe_2O_3 produced—

$$2K_2FeO_4 + 2NH_3 = N_2 + Fe_2O_3 + 4KHO + H_2O.$$

D. BARIUM FERRATE ($BaFeO_4$).—This compound is prepared by double decomposition, by precipitating potassium ferrate with barium nitrate or barium chloride, an insoluble precipitate of a handsome purple-red colour being formed.

It is much more stable than the alkali ferrates, and is but slightly affected by organic substances. Powerful acids expel oxygen and form the corresponding barium and ferric salts.

With acetic acid it gives a handsome red solution, which is decolorised on heating.

The ferrates of calcium and strontium are also insoluble, and are obtained by the double decomposition method.

42. **Sulphides of Iron.**—These compounds, which are more numerous than the oxides, will now be dealt with in succession, commencing with those containing least sulphur.

A. IRON SUB-SULPHIDE (Fe_8S).—This substance, described by Arfvedson, is formed on the reduction of basic ferric sulphate by hydrogen. It is a dull dark grey powder, which dissolves in acids, with evolution of $\frac{6}{7}$ H and $\frac{1}{7}$ H_2S.

B. IRON SUB-SULPHIDE (Fe_2S).—This sulphide has been prepared by reducing anhydrous ferrous sulphate by hydrogen. In the initial stage SO_2 and H_2O are obtained, and subsequently H_2S.

The reaction may be explained by one or other of the following equations:—

$$(1)\quad 2SO_4Fe + 9H_2 = Fe_2S + H_2S + 8H_2O.$$

$$(2)\quad 4SO_4Fe + 15H_2 = 2Fe_2S + H_2S + SO_2 + 14H_2O.$$

When treated with H_2S in the warm, this sulphide, like the preceding one, is converted into magnetic pyrites.

C. FERROUS SULPHIDE (FeS) is obtained by mixing together 60 parts of iron filings and 40 parts of sulphur with sufficient hot water to form a paste (Lemery's volcano), combination being attended by evolution of heat. The resulting sulphide is readily oxidised.

Crystalline FeS is obtained by the action of H_2S on ferroferric oxide, H_2O and H_2S being liberated. If stronger heat is applied sulphur is evolved, and black or yellow hexagonal crystals are left (Sidot). On heating 56 parts of iron with 32 parts of sulphur, a porous, black, somewhat fusible mass is obtained, the principal use of which is for preparing H_2S in the laboratory.

FeS may also be prepared by the wet method by precipitating a ferrous salt with an alkali sulphide—

$$SO_4Fe + Na_2S = FeS + SO_4Na_2,$$

or with a bisulphide—

$$SO_4Fe + 2NaHS = FeS + H_2S + SO_4Na_2.$$

When ferric salts are employed, FeS is also formed, but in this case sulphur is deposited—

$$(SO_4)_3Fe_2 + 3Na_2S = 3SO_4Na_2 + 2FeS + S.$$

The higher sulphides of iron when heated to bright redness part with sulphur, a residue of FeS being left.

The precipitated sulphide, FeS, is black, insoluble in water, but dissolves in acids without yielding any deposit of sulphur or disengaging free hydrogen; it is also soluble in alkalis. This sulphide is readily oxidised, and turns grey in consequence of the liberation of part of its sulphur; at the same time, ferrous sulphate and ferric oxide are formed—

$$6FeS + 7O_2 = 2SO_4Fe + 2Fe_2O_3 + 2S_2.$$

Ferrous sulphide prepared by the dry method is fusible, brittle, and undecomposable by even white heat, or by hydrogen, carbon, etc. If, however, lime, earthy carbonates or silicates are present, it is decomposed by carbon.

In contact with nitric acid, FeS liberates NO, and yields Fe_2O_3 and H_2SO_4.

Ferrous sulphide is comparatively rare in nature.

D. MAGNETIC PYRITES (Fe_7S_8).—This pyrites may be regarded as a saline sulphide formed by the union of the sesquisulphide or the bisulphide of iron with ferrous sulphide—

$$FeS_2, 6FeS, \text{ or } Fe_2S_3, 5FeS.$$

It is obtained artificially by calcining the bisulphide, or by treating iron at white heat with sulphur; or again, by dropping sulphur into a red-hot crucible charged with iron turnings.

There is also another sulphide, Fe_3S_4, corresponding to the magnetic oxide Fe_3O_4, and to which the name "magnetic pyrites" is better applicable than to Fe_7S_8.

According to Rammelsberg, a sulphide with the formula Fe_5S_6 can be prepared by bringing incandescent iron into contact with sulphur.

E. IRON SESQUISULPHIDE (Fe_2S_3).—This sulphide is formed by heating to dark redness a mixture of sulphur and ferrous sulphide; and also by passing a current of H_2S over Fe_2O_3 heated to about 100° C.

In the anhydrous condition it is unalterable by air, is of a yellowish-grey colour with a green or greyish tinge, and is partially soluble in acids.

It occurs in nature, frequently in association with copper as coppery pyrites, CuS, Fe_2S_3, and sometimes as $3CuS, Fe_2S_3$.

F. IRON BISULPHIDE, (syn.: Iron pyrites) (FeS_2).—This, the most important sulphide of iron, may be produced artificially by gently heating iron with an excess of sulphur. Wöhler has obtained it, in the form of octahedral crystals, by heating a mixture of ferric oxide, sulphur, and sal ammoniac on the sand bath; and it may also be prepared by the action of sulphuretted hydrogen on ferric oxide, ferro-ferric oxide, or ferrous carbonate, at a temperature between 100° C. and dark red heat. Below 100° C. the product mainly consists of sesquisulphide, and above red heat of magnetic pyrites.

When heated in the air the bisulphide gives off sulphur dioxide and leaves behind ferrous sulphate—or a basic ferric sulphate, if the temperature is high enough to effect the decomposition of the ferrous sulphate.

If heated in a current of phosphuretted hydrogen to a temperature below that at which sulphur is liberated spontaneously, the bisulphide yields iron phosphide, sulphur and sulphuretted hydrogen being disengaged.

This sulphide is very abundant in nature, and constitutes ordinary or martial pyrites, which occurs in two allotropic modifications.

(1) *Cubical Pyrites* is of a brassy-yellow colour, with a sp. gr. = 4·8 to 5·2. It gives off sparks when struck against steel.

(2) *Prismatic Pyrites.*—This form, which is less common, is white, and of sp. gr. 4·74. Wöhler mentions that these two densities exhibit the same mutual ratio as those of octahedral and prismatic sulphur (2·066 and 1·962).

G. IRON PERSULPHIDE (FeS_3).—Like ferric anhydride, this sulphide has not yet been isolated, though it is known in a state of soluble combination with potassium sulphide, the compound being prepared by passing H_2S through a solution of potassium ferrate.

43. **Nitrosulphides of Iron.**—These salts, discovered by Roussin, constitute a remarkable group of substances, in which the contained iron cannot be detected by any of the usual reagents, as is also the case with the ferrocyanides.

The nature of these compounds is still the subject of controversy; and the researches of Porczinsky, Rosenberg, Pawel, and Demel have increased the complexity of the question by the varying formulæ arrived at by these authors, according to the methods of preparation employed. According to Roussin, if two solutions, one of ammonium bisulphide, the other of potassium nitrite, be mixed together and treated with ferric chloride or ferric sulphate, added drop by drop with continual agitation, on heating to ebullition the blackish precipitate is re-dissolved. On filtration after boiling, the very dark coloured filtrate obtained deposits, on cooling, a large quantity of black crystals, whilst sulphur is left on the filter. The reaction is equally well defined when ferrous sulphate is employed, but there is no longer any deposit of sulphur; and if a slight excess of alkali sulphide has been taken, the precipitate re-dissolves almost completely.

Porczinsky works in a slightly different manner, by adding ammonium bisulphide to a solution of ferrous sulphate saturated with nitrogen dioxide, heating to 100° C., filtering, and evaporating the filtered liquid.

Demel proceeds by adding 1 c.c. of ammonium bisulphide solution to 20 grams of potassium nitrite dissolved in 300 c.c. of boiling water. Ebullition having been continued for several minutes, a solution of 33 grams of ferrous sulphate in 200 c.c. of water is added.

Pawel adds 10 grams of sodium sulphide, dissolved in 300 c.c. of water, to a boiling solution of 40 grams of potassium nitrite in 600 c.c. of water. He then introduces 70 grams of ferrous sulphate dissolved in 300 c.c. of water, heats to 70° to 80° C. for half an hour, and leaves to cool after filtration.

The crystals deposited when the cooling down has been gradual are usually very well formed and sometimes attain 1 to 2 cm. in length. They are very heavy, easy to wash, and sparingly soluble in cold water, but more readily so in hot; very soluble in alcohol, glacial acetic acid, amyl alcohol, and slightly soluble in petroleum spirit and in turpentine. In ordinary ether they are soluble in all proportions, and are instantly liquefied by contact with the vapour of this solvent, but are totally insoluble in CS_2.

The crystals are of a very dark colour, with a metallic lustre, and greatly resemble iodine. Their tinctorial power is very considerable, and the flavour is styptic at first, subsequently becoming bitter.

Provided they have been deposited from a slightly alkaline liquor, they are unalterable on exposure to air. Decomposition does not ensue on heating, until the temperature reaches 115° to 140° C.

Concentrated sulphuric, nitric, and hydrochloric acids attack them briskly at the ordinary temperature; and ammonia precipitates them from their solutions, as do also $(NH_4)_2S$, H_2S, and the ferro- and ferri-cyanides; tannins, however, have no action.

With silver nitrate a black precipitate of sulphide and ferric sulphide is formed, nitrogen dioxide being liberated; but gold chloride is reduced to the metallic state.

The formulæ ascribed by different authors to the compounds obtained, by methods differing but slightly one from another, are very dissimilar. Thus Roussin styles his product "iron dinitrosulphide," and assigns it the following composition:—

$$Fe_3S_5H_2(NO)_4 = Fe_2S_5(NO)_3.H_2S.FeS.NO.$$

That obtained by Porczinsky is credited with being

$$Fe_3S_3(NO)_4, 2H_2O = FeS, Fe_2S_2(NO)_4 + 2H_2O.$$

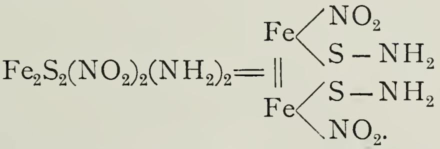
Rosenberg's nitrosulphide corresponds to the formula

$$Fe_6S_5(NO)_{10}, 4H_2O;$$

whilst Pawel gives the symbol as

$$Fe_7S_5(NO)_{12}H_2.$$

Demel has described the ammonium compound of the nitrosulphide obtained by himself, and considers it as a nitrated amide of the composition



$$Fe_2S_2(NO_2)_2(NH_2)_2 = \begin{array}{l} Fe\left\langle \begin{array}{l} NO_2 \\ S-NH_2 \end{array} \right. \\ \| \\ Fe\left\langle \begin{array}{l} S-NH_2 \\ NO_2. \end{array} \right. \end{array}$$

Caustic potash and soda have no action on iron dinitrosulphide in the cold; but, on prolonged ebullition, ammonia is liberated, and a red crystalline deposit of ferric hydrate, $Fe_2H_2O_4$, is formed, leaving a less highly coloured liquid, which, when concentrated over sulphuric acid, furnishes voluminous black crystals arranged like a series of hoppers.

The crystals obtained by the action of caustic soda have received from Roussin the name of "sulphuretted nitrosulphide of iron and sodium" (*nitrosulfure sulfuré de fer et de sodium*), and consist of

$$Fe_2S_3(NO)_2, 3Na_2S + aq.$$

Porczinsky gives to this compound, when dried at 100° C., the formula

$$Na_2S, Fe_2S_2(NO)_4;$$

whilst, according to Rosenberg, the formula of the crystals should be

$$Fe_8S_9(NO)_{18}Na_8 + 24H_2O;$$

or, according to Pawel,

$$Fe_{10}S_{10}(NO)_{18}Na_{10} + 27H_2O.$$

The crystals are soluble in water or alcohol, but insoluble in ether. When dissolved and heated with lead nitrate they yield a reddish precipitate soluble in caustic potash; whilst zinc sulphate gives a brown precipitate containing zinc, sulphur, iron, and nitrogen dioxide. Ferric chloride gives a black precipitate, but none is produced by tannin, sulphuretted hydrogen, and potassium ferrocyanide; whilst the ferricyanide gives a precipitate of Prussian blue.

When treated with acids, in the cold, the solution yields a flocculent reddish precipitate, which readily parts with sulphuretted hydrogen, and which exhibits the composition $Fe_2S_3(NO)_2$, $4H_2S$. Roussin terms this substance "sulphuretted nitrosulphide of iron" (*nitrosulfure sulfuré de fer*).

If a boiling solution of the above-named crystals be treated with dilute acid, H_2S is disengaged, and a dense black deposit, insoluble in water, alcohol, or ether, is formed containing $Fe_2S_3(NO)_2$, *i.e.* iron nitrosulphide. This is a very inflammable substance, and decomposes gradually in the dry state. With sodium sulphide it gives large crystals, red by transmitted light, black by reflection, soluble in water, alcohol, or ether, but insoluble in carbon disulphide or chloroform; the composition is represented by $Fe_2S_3(NO)_2$, Na_2S, H_2O. On treating a solution of this salt with an acid, iron nitrosulphide is reconstituted.

The iron nitrosulphide compounds may be compared to the nitrocyanides, into which, moreover, they can be converted under the influence of mercury cyanide or potassium cyanide. Conversely, the nitrocyanides may be transformed into nitrosulphides by the acid of sulphuretted hydrogen or an alkali sulphide.

44. **Sulphites of Iron.**—*A.* FERROUS SULPHITE ($SO_3F, 3H_2O$).—When iron is dissolved by sulphurous acid, out of contact with air, a liquid is obtained containing both SO_3Fe and S_2O_3Fe, from which, on evaporation *in vacuo*, ferrous sulphite separates out in the form of greenish needles containing $3H_2O$. This sulphite oxidises readily in presence of moist air; it is sparingly soluble in cold water, the solubility increasing in presence of SO_2.

B. FERRIC SULPHITE, $(SO_3)_3Fe$, is unknown in the solid state, and the solution is very unstable.

When ferric hydrate is dissolved in sulphurous acid the liquid acquires a red colour at first, but afterwards becomes rapidly decolorised in consequence of the formation of ferrous sulphate—

$$(SO_3)_3Fe_2 = SO_4Fe + SO_3Fe + SO_2.$$

Solutions of ferric sulphite yield, on boiling, an insoluble ochreous powder of basic sulphite—

$$(Fe_2O_3)_3SO_2, 7H_2O.$$

If alcohol be added, instead of boiling the solution, a basic sulphite is also thrown down.

45. **Ferrous Hyposulphite** (S_2O_3Fe) is obtained as a residue in the preparation of ferrous sulphite, or by double decomposition between barium hyposulphite and ferrous sulphate; or again, by digesting sulphur with ferrous sulphite. It takes the form of small greenish needles soluble in alcohol.

46. **Thiosulphates of Iron.**—*A.* FERROUS THIOSULPHATE ($S_2O_6Fe, 5H_2O$).—This is obtained by double decomposition between barium thiosulphate and ferrous sulphate, the filtered liquid yielding, on spontaneous evaporation, small greenish prisms, oxidising on exposure to air and soluble in water.

B. FERRIC THIOSULPHATE ($(S_2O_6)_3Fe_2$).—When thiosulphuric acid is treated with ferric hydrate a basic thiosulphate is obtained as a brown-red powder.

The thiosulphate $(S_2O_6)_3Fe_2$ is obtained, as a red solution, by double decomposition.

47. **Ferrous Tetrathionate** (S_4O_6Fe) is a very unstable salt, readily decomposing into ferrous sulphate, sulphuric acid, and sulphur. It is prepared by adding ferrous hyposulphite, drop by drop, to a solution of Fe_2Cl_6—

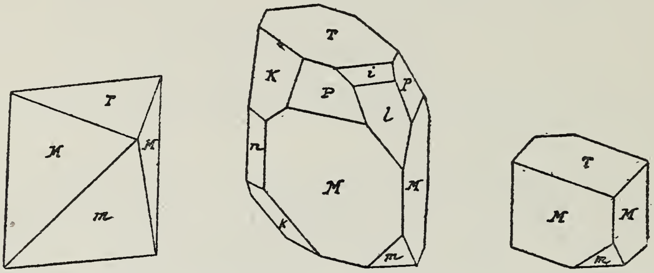
$$Fe_2Cl_6 + 2S_2O_3Fe = 3FeCl_2 + S_4O_6Fe.$$

48. **Sulphates of Iron.**—*A.* FERROUS SULPHATES.—I. *Normal Ferrous Sulphate* ($SO_4Fe, 7H_2O$).—This substance, which is still known as *green vitriol*, *green copperas*, etc., is one of the most important salts of iron.

It is prepared, on a manufacturing scale, by the action of sulphuric acid on iron, by oxidising pyrites, pyritic shales, etc.

The product is, however, impure, being contaminated with copper, tin, zinc, manganese, alumina, magnesia, lime, silica, sulphuric acid, organic matter, etc.

In the laboratory, ferrous sulphate is prepared by treating an excess of iron with pure H_2SO_4, or by repeatedly re-crystallising the commercial salt.



FIGS. 33, 34, and 35.—The forms most commonly assumed by ferrous sulphate.

Ferrous sulphate crystallises in the oblique prismatic system, as rhomboidal crystals of a bluish-green colour, containing $7H_2O$. They exhibit a disagreeable styptic flavour, and a sp. gr. = 1·884.

This salt is soluble in water, 100 parts of crystals dissolving

At 10° C. in 164 parts of water.
,, 15° ,, 143 ,, ,,
,, 24° ,, 87 ,, ,,
,, 43° ,, 66 ,, ,,

At 60° C. in 38 parts of water.
,, 90° ,, 27 ,, ,,
,, 100° ,, 30 ,, ,,

The density of various solutions of this salt at 17·2° C. is given in the subjoined table (R. Jagnaux):—

Density.	$SO_4Fe,7H_2O$ per cent.	SO_4Fe per cent.	Density.	$SO_4Fe,7H_2O$ per cent.	SO_4Fe per cent.	Density.	$SO_4Fe,7H_2O$ per cent.	SO_4Fe per cent.	Density.	$SO_4Fe,7H_2O$ per cent.	SO_4Fe per cent.
1·0052	1	0·547	1·0605	11	6·017	1·1214	21	11·487	1·1876	31	16·957
1·0105	2	1·094	1·0664	12	6·564	1·1278	22	12·034	1·1945	32	17·504
1·0158	3	1·641	1·0723	13	7·111	1·1343	23	12·581	1·2014	33	18·051
1·0212	4	2·188	1·0782	14	7·658	1·1408	24	13·128	1·2084	34	18·598
1·0266	5	2·735	1·0842	15	8·205	1·1473	25	13·675	1·2154	35	19·145
1·0321	6	3·282	1·0903	16	8·752	1·1539	26	14·222	1·2225	36	19·692
1·0377	7	3·829	1·0964	17	9·299	1·1606	27	14·769	1·2296	37	20·239
1·0433	8	4·376	1·1026	18	9·846	1·1673	28	15·316	1·2368	38	20·786
1·0490	9	4·923	1·1088	19	10·393	1·1740	29	15·863	1·2440	39	21·333
1·0547	10	5·470	1·1157	20	10·940	1·1808	30	16·410	1·2513	40	21·880

According to Gerlach, the density of ferrous solutions at 15° C. is as follows:—

Density.	$SO_4Fe, 7H_2O$.	Density.	$SO_4Fe, 7H_2O$.
1·011	2 per cent.	1·082	15 per cent.
1·021	4 ,,	1·112	20 ,,
1·032	6 ,,	1·143	25 ,,
1·043	8 ,,	1·174	30 ,,
1·054	10 ,,	1·206	35 ,,
1·065	12 ,,	1·239	40 ,,

Ferrous sulphate is almost insoluble in strong alcohol, and entirely so in glacial acetic acid, though soluble to the extent of about 3 grams per litre in 50° alcohol.

On heating, the crystallised salt melts in its own water, and afterwards gradually suffers dehydration. At 100° C. it parts with 6 molecules of water, but the final molecule is not driven off until nearly 300° C. is attained. This seventh molecule of water seems to play a different part to the rest, since it is more difficult to eliminate. This it is also which proves the existence of double salts, such as

$$(SO_4)_2K_2Fe, 6H_2O,$$

isomorphous with $SO_4Fe, 7H_2O$, and which may be regarded as derived from the latter by the substitution of 1 mol. of K_2SO_4 for 1 mol. of water.

At red heat, ferrous sulphate splits up into SO_2, SO_3, and Fe_2O_3—

$$2SO_4Fe = Fe_2O_3 + SO_3 + SO_2.$$

In the crystallised state, ferrous sulphate is somewhat unstable, oxidising on exposure to the air, and turning yellow, with formation of an external ochreous layer of basic ferrous sulphate containing $(SO_4)_3Fe_2, 5Fe_2O_3$ or $(Fe_2O_3)_2SO_3$. This oxidised salt is the one employed in the manufacture of Nordhausen sulphuric acid.

To preserve ferrous sulphate unaltered in the laboratory, the addition of glucose or gum, to the mother liquor from which the crystals are to be deposited, has been proposed. For the same purpose Welborn recommends that a fragment of camphor wrapped in paper should be kept with the crystals; the keeping properties are also improved by their containing a little free sulphuric acid, as also by their being stored in a perfectly dry state and in a dry atmosphere.

In solution also, ferrous sulphate is oxidised by exposure to the air, and becomes turbid, depositing basic salts. It may, however, be preserved indefinitely by an addition of sulphuric acid and exposure to sunlight.

When a solution of ferrous sulphate is exposed to the air it deposits an ochreous powder, $(Fe_2O_3)_2SO_3$, $3H_2O$. The solution then contains, in addition to ferrous sulphate, normal ferric sulphate, $(SO_4)_3Fe_2$, and a basic sulphate, $(SO_4)_3Fe_2$, Fe_2O_3. The composition of the precipitate, however, is by no means constant, but varies according to the strength of the solution, duration of exposure to air, etc.

On adding water, a new precipitate of varying composition is thrown down, leaving a ferro-ferric sulphate in solution.

Dissolved ferrous sulphate readily absorbs nitrogen dioxide, the liquid then becoming a dark blackish brown. On evaporating the solution *in vacuo*, NO is disengaged; if heat be applied, nitrous oxide is liberated and ferric sulphate formed. When heated to boiling, the solution suddenly decomposes after a while, with considerable effervescence, reddish fumes being evolved if a slight excess of nitric acid be present. Treated by alkalis in the warm, ammonia is formed; and when heated with absolute alcohol until the precipitate ceases to re-dissolve, very unstable brown crystals are obtained on cooling down the mixture out of contact with air. With an excess of alcohol a more stable brown precipitate is produced.

Ferrous sulphate is affected by all oxidising agents, nitric acid converting it into ferric sulphate. Chlorine also acts as an oxidiser, without any formation of basic salts taking place—

$$6SO_4Fe + 3Cl_2 = Fe_2Cl_6 + 2(SO_4)_3Fe_2.$$

Crystallised ferrous sulphate dissolves in 400 molecules of water, 4510 calories being absorbed per molecule of the salt.

In the normal state, ferrous sulphate contains 7 molecules of water and is isomorphous with the magnesium series; but under certain conditions it parts with varying proportions of its water of crystallisation, and furnishes hydrates containing 1, 2, 3, 4, etc., molecules of water, or the anhydrous salt.

II. *Anhydrous Ferrous Sulphate* (SO_4Fe).— This salt is a greyish-white powder, obtained by exposing the hydrated sulphate to a temperature of about 300° C. When brought into contact with water it becomes hydrated, and recovers its green colour.

III. *Ferrous Sulphate with* 1 *Molecule of Water of hydration* (SO_4Fe, H_2O) is obtained by heating the ordinary hydrated salt to about 140° C. It loses its water towards 300° C.

IV. *Ferrous Sulphate with* 2 *Molecules of Water* ($SO_4Fe, 2H_2O$).—According to Bonsdorff, this salt is obtained by treating a saturated solution of ferrous sulphate with sulphuric acid, added by degrees—so as not to unduly raise the temperature—until the density of the liquid has attained 1·33. On allowing the solution to evaporate, crystals of sulphate containing $4H_2O$ are formed at first, whilst the final crop of crystals exhibits the formula $SO_4Fe, 2H_2O$.

V. *Hydrated Sulphate with* 3 *Molecules of Water* ($SO_4Fe, 3H_2O$).—When ferrous sulphate is crystallised in HCl the salt $SO_4Fe, 3H_2O$ is obtained on cooling. It may also be prepared, as a white incrustation, by evaporating a solution of $SO_4Fe, 7H_2O$, strongly acidified by H_2SO_4.

VI. *Hydrated Sulphate with* 4 *Molecules of Water* ($SO_4Fe, 4H_2O$).—According to Regnault, this hydrate is formed when a solution of ferrous sulphate is crystallised at 80° C.

The author has found this salt, mixed with a little basic ferric sulphate, aluminium sulphate, calcium sulphate, etc., as an accidental evaporation product of the liquors employed in the manufacture of alum and ferrous sulphate from pyritic lignites. He has also obtained it in the laboratory by subjecting a concentrated solution of ferrous sulphate, slightly acidified with H_2SO_4 to prolonged boiling, the water being replaced as evaporated. It forms a dense, greenish-white crystalline powder, which becomes re-hydrated on contact with water, and sets like plaster of Paris. It crystallises in the monoclinic system.

VII. *Hydrated Sulphate with* 5 *Molecules of Water* ($SO_4Fe, 5H_2O$).—This salt, which crystallises in triclinic crystals, has been prepared by Marignac by evaporating an acidified solution of ferrous sulphate *in vacuo*. The crystals first formed contain $7H_2O$, followed by those containing $5H_2O$, and finally by a crop having only 4 molecules of water.

VIII. *Hydrated Sulphate with 6 Molecules of Water* (SO_4Fe, $6H_2O$) is obtained by crystallising ferrous sulphate in hydrochloric acid through which a current of gaseous HCl is being passed. Owing to the action of the air the sulphate is partially converted into chloride, Fe_2Cl_4, which crystallises out. The mother liquor deposits tabular crystals of SO_4Fe, $6H_2O$.

IX. *Ferrous Anhydrosulphate* (S_2O_7Fe).—This is a hygroscopic white powder, which comes down on the addition of $9H_2SO_4$ to 1 volume of aqueous solution of ferrous sulphate.

X. *Acid Ferrous Sulphate.*—Bonsdorff claims to have obtained, in the preparation of the hydrated sulphate containing $2H_2O$, an acid sulphate containing

Ferrous oxide	28·38	per cent.
Sulphuric acid	45·42	,,
Water	25·97	,,

XI. *Ferro-potassium Sulphate*, $(SO_4)_2K_2Fe$, $6H_2O$, is obtained by dissolving iron in potassium bisulphate. It forms greenish clinorhombic prisms, of sp. gr. 2·189. In presence of an excess of H_2SO_4, crystals with $4H_2O$ are obtained; at 60° C. the crystals formed contain $2H_2O$.

XII. *Ferro-sodium Sulphate* is less stable than the foregoing compound. It is prepared by crystallising the mixture of the two sulphates at over 35° C., the resulting crystals being clinorhombic and containing $4H_2O$.

XIII. *Ferro-ammonium Sulphate.*—To prepare this salt, equivalent proportions of the two sulphates are crystallised together; the resulting crystals have the formula $(SO_4)_2(NH_4)_2Fe$, $6H_2O$. They are voluminous, of a pale green colour, sp. gr. 1·813, and less subject than ferrous sulphate to alteration on exposure to the air.

The conjoint action of concentrated hydrochloric acid and air converts this salt into ferri-ammonium chloride.

The density of various solutions of ferro-ammonium sulphate is given in the following table:—

Density.	$(SO_4)_2(NH_4)_2Fe, 6H_2O$.	Density.	$(SO_4)_2(NH_4)_2Fe, 6H_2O$.
1·021	4 per cent.	1·070	12 per cent.
1·030	6 ,,	1·090	15 ,,
1·045	8 ,,	1·111	20 ,,
1·055	10 ,,	1·163	33·33 ,,

Ferrous sulphate forms other double salts, notably with the sulphates of zinc, copper, etc., as well as with the sulphates isomorphous with aluminium sulphate. These bodies are, however, frequently regarded as simple mixtures.

XIV. *Ferrous Sulphate and Zinc Sulphate.*—The two salts crystallise together, and if the mixture contains at least 15 per cent. of ferrous sulphate the crystals resemble those of that salt. If, on the other hand, zinc sulphate predominates, the crystals are modified accordingly, and take the form assumed by this sulphate.

XV. *Ferrous Sulphate and Copper Sulphate.*—When ferrous sulphate predominates the crystals take the ferrous sulphate form, and contain $7H_2O$; in the contrary event they resemble those of copper sulphate, and contain $5H_2O$.

XVI. *Ferro-ferric Sulphates.*—Ferrous sulphate and ferric sulphate form between them certain well defined double salts.

When a cold solution containing 3 molecules of ferrous sulphate and 2 molecules of ferric sulphate is treated with concentrated sulphuric acid an unstable precipitate containing

$$(SO_4)_9Fe_3(Fe_2)_2, 4H_2O$$

is formed.

On diluting a solution of the two sulphates with 5 or 6 times its weight of water, the temperature rises by 25°, and, on re-cooling, long pale green prisms corresponding to

$$SO_4Fe + 6[(SO_4)_3Fe_2] + 10H_2O$$

are deposited.

When a concentrated solution of the two sulphates is treated with a large excess of H_2SO_4, and cooled down after heating to about 200° C., it furnishes rose-coloured hexagonal crystals of an acid ferro-ferric sulphate containing

$$(SO_4)_3Fe_2, SO_4Fe, 2H_2SO_4.$$

B. FERRIC SULPHATES.—I. *Normal Ferric Sulphate*, $(SO_4)_3F_2$, may be prepared by dissolving ferric hydrate in sulphuric acid, or by gradually adding to a solution containing nitric and sulphuric acids a quantity of ferrous sulphate corresponding to 2 molecules per each molecule of H_2SO_4—

$$6(SO_4Fe, 7H_2O) + 3H_2SO_4 + 2HNO_3$$
$$= 3[(SO_4)_3Fe_2] + 2NO + 46H_2O.$$

On evaporating to dryness, to drive off the excess of HNO_3, a yellowish-white residue of normal ferric sulphate is left. This product is insoluble in HCl, but dissolves slowly in water and becomes hydrated. Iron and analogous metals reduce it to the condition of ferrous sulphate, with evolution of hydrogen, and it is broken up by heat into SO_3 and Fe_2O_3.

When boiled, ferric sulphate solution is partially decomposed and throws down a basic hydrated salt. Alkali carbonates precipitate a body which re-dissolves, with effervescence, on agitation, the highly coloured liquid then gradually depositing a yellow precipitate of basic sulphate.

When alcohol is added to a solution of ferric sulphate containing a little potassium carbonate, normal sulphate remains in solution, and an unstable reddish-yellow saline mass of a complex ferri-potassium sulphate is thrown down. This decomposes after a while, yielding an insoluble basic ferric sulphate.

Hydrated ferric sulphate is of a dark brown colour, and normally contains $9H_2O$, in which state it is found native in Chili. A hydrated sulphate containing $10H_2O$ has been obtained in the form of nacreous rhomboidal lamellæ, by peroxidising ferrous sulphate with HNO_3 and boiling with an excess of sulphuric acid.

Ferric sulphate is extremely soluble in water, the density of its solutions, measured at 17·5° C., being given in the following table.

Several basic ferric sulphates are known, and the general method adopted for their preparation is by the action of oxidising agents on ferrous sulphate in the same way as for the normal sulphate. In treating of the valency of iron it was admitted that the double hexatomic molecule (Fe_2) results from the junction of 2 atoms Fe playing the part of a tetravalent body, and that, consequently, ferric chloride may be regarded as $Cl_3Fe - FeCl_3$. Now, normal ferric sulphate has the formula $(SO_4)_3Fe_2$, and the basic sulphates may be considered as this normal salt, wherein 1 or 2 divalent atoms of oxygen have replaced 1 or 2 divalent groups SO_4.

Density.	$(SO_4)_3Fe_2$.	Density.	$(SO_4)_3Fe_2$.
1·0170	2 per cent.	1·3368	32 per cent.
1·0340	4 ,,	1·3646	34 ,,
1·0512	6 ,,	1·3927	36 ,,
1·0684	8 ,,	1·4217	38 ,,
1·0854	10 ,,	1·4506	40 ,,
1·1042	12 ,,	1·4824	42 ,,
1·1230	14 ,,	1·5142	44 ,,
1·1420	16 ,,	1·5468	46 ,,
1·1624	18 ,,	1·5808	48 ,,
1·1826	20 ,,	1·6148	50 ,,
1·2066	22 ,,	1·6508	52 ,,
1·2306	24 ,,	1·6868	54 ,,
1·2559	26 ,,	1·7241	56 ,,
1·2825	28 ,,	1·7623	58 ,,
1·3090	30 ,,	1·8006	60 ,,

II. *Basic Ferric Sulphate* (Fe_2O_3, $2SO_3 = Fe_2\left\{\begin{matrix}(SO_4)_2\\ O\end{matrix}\right.$).—The body is obtained from the normal sulphate by partial neutralisation with calcium carbonate until the resulting precipitate becomes permanent. The filtered liquid then contains in solution $Fe_2\left\{\begin{matrix}(SO_4)_2\\ O\end{matrix}\right.$.

It may also be prepared by digesting normal ferric sulphate with ferric hydrate, the resulting red liquid yielding, on desiccation, an uncrystallisable gummy mass. This salt decomposes on the solution being diluted or boiled, an insoluble basic salt being thrown down and normal sulphate left in solution.

O. Meister described a hydrate of this body deposited as clinorhombic crystals from a mordant used in dyeing. They were but sparingly soluble in the cold, and decomposed when boiled. The formula was $2SO_3$, Fe_2O_3, $15H_2O$, and 12 out of the 15 molecules of water were eliminated at 100° C.

According to S. Umfreville Pickering, the only basic sulphate of well defined composition obtained by the action of water on

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the normal sulphate is $2SO_3, Fe_2O_3$. This sulphate forms double salts with the alkali sulphates, for which its affinity is greater than the normal sulphate, since it displaces the latter from the alums.

III. *Basic Sulphate* ($5SO_3, 3Fe_2O_3 = (Fe_2)_3\left\{\begin{matrix}(SO_4)_5\\ O_4\end{matrix}\right.$).—This compound is prepared by regulating the action of HNO_3 on a mixture of ferrous sulphate and H_2SO_4, a fresh addition of ferrous sulphate being made as soon as the evolution of nitrous fumes has ceased. The resulting dark red solution is unstable in presence of water, which breaks it up into normal sulphate and the basic salt.

IV. *Basic Sulphate* $(Fe_2O_3)_2(SO_3)_5 = (Fe_2)_2\left\{\begin{matrix}(SO_4)_5\\ O\end{matrix}\right.$.—A dark solution of this salt is produced by gradually adding boiling ferrous sulphate to a mixture containing HNO_3 and H_2SO_4 in suitable proportions; a little sub-salt separates during the operation. A similar solution of basic ferric sulphate (known in France as "*Rouil*"), largely employed as a mordant in dyeing, and the manufacture of which will be examined in detail later on, is prepared on a large scale in the same way, so as to obtain the same ratio of Fe and SO_4 as in $(Fe_2)_2\left\{\begin{matrix}(SO_4)_5\\ O\end{matrix}\right.$.

V. *Basic Sulphate* $(Fe_2)_2\left\{\begin{matrix}SO_4\\ O_2\end{matrix}\right.$.—This is obtained, as a red flocculent precipitate, by boiling a solution of ferri-potassium sub-sulphate; it contains $3H_2O$.

VI. *Sulphate*, $(Fe_2)_2\left\{\begin{matrix}SO_4\\ O_5\end{matrix}\right.$, is formed by the action of air on ferrous sulphate, or by an incomplete precipitation of ferric sulphate with an alkali. Another way is by heating a dilute solution of normal sulphate. The precipitate is red, turning yellow on desiccation, and brown when anhydrous. This sub-salt is employed for painting on porcelain.

VII. *Sulphate* $(Fe_2)_4\left\{\begin{matrix}SO_4\\ O_{11}\end{matrix}\right.$.—According to Anthon, this salt is produced by precipitating the normal sulphate with barium acetate, barium sulphate being formed along with yellowish flakes which can be separated by levigation.

VIII. *Sulphate,* $(Fe_2)_7\left\{\begin{matrix}SO_4\\O_{20}\end{matrix}\right.$, has been found at Modum (Norway) as a hydrated brown mass.

IX. *Sulphate* $(Fe_2)_7\left\{\begin{matrix}(SO_4)_{12}\\O_9\end{matrix}\right.$.—In analysing a deposit of ochre-yellow basic salt produced in the manufacture of the above-named basic mordant (*Rouil*), the author obtained the following proportions of ferric oxide and sulphur trioxide, after washing and desiccation in air :—

	Found.	Calculated.
SO_3 . . .	37·80	37·38
Fe_2O_3 . .	43·20	43·62
	81·00	81·00

which correspond to the formula

$$12SO_3,\ 7Fe_2O_3 = (Fe_2)_7\left\{\begin{matrix}(SO_4)_{12}\\O_9\end{matrix}\right..$$

C. DOUBLE SALTS.—I. *Ferri-ammonium Alum* (iron alum), $(SO_4)_3Fe_2$, $SO_4(NH_4)_2$, $24H_2O$.—Cubo-octahedral crystals, or octahedra, of iron alum (sp. gr. 1·712), are obtained by allowing a mixture of ammonium sulphate and normal ferric sulphate to crystallise from aqueous solution.

II. *Ferri-potassium Alum* may be prepared by crystallising a mixture of the component sulphates, or by adding HNO_3 to a solution containing 2 molecules of ferrous sulphate, 1 molecule of potassium sulphate, and 1 molecule of H_2SO_4. Also by treating a mixture of KNO_3 and SO_4Fe, $7\ H_2O$ with H_2SO_4, crystals of iron alum are obtained. They take the form of regular octahedra, are often of considerable bulk, and are of an amethyst-violet shade.

The following table gives the densities of solutions of this alum, measured at 17·5° C.

Density.	Alum.	Density.	Alum.	Density.	Alum.
1·0108	2 per cent.	1·0548	12 per cent.	1·0990	22 per cent.
1·0216	4 ,,	1·0630	14 ,,	1·1086	24 ,,
1·0308	6 ,,	1·0716	16 ,,	1·1136	26 ,,
1·0386	8 ,,	1·0804	18 ,,	1·1320	28 ,,
1·0466	10 ,,	1·0894	20 ,,	1·1422	30 ,,

III. *Various Double Salts.*—Double basic salts, such as

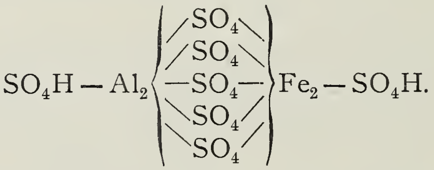
$$2(SO_4K_2),\ Fe_2O_3,\ 2SO_3,\ 6H_2O,$$
$$2(SO_4(NH_4)_2),\ Fe_2O_3,\ 2SO_3,\ 6H_2O,$$
$$5(SO_4K_2),\ (Fe_2O_3)_3,\ (SO_3)_7,\ 21H_2O,$$

may be obtained either by the action of ammonia on ammoniacal or potassic iron alum, or by calcining these alums.

The salt SO_4K_2, $4Fe_2O_3$, SO_3, $9H_2O$ has been found as ochreous masses in Bohemian lignites; and pale yellow masses of the corresponding sodium salt are met with in the aluminous schists of Modum (Norway).

A large number of double ferric salts, both of normal and acid character, resulting from the union of 2 sesquisulphates, have been brought to our knowledge by Etard. In order to prepare them, he dissolves these sesquisulphates in a large excess of H_2SO_4, and applies heat, accompanied by agitation, until a precipitate is formed. This is collected on glass wool and washed with cold sulphuric acid, followed by glacial acetic acid.

Ferri-aluminium sulphate occurs as microscopic, white, hexagonal lamellæ, which are insoluble in water, and are gradually decomposed thereby. The formula of this salt is $(Al_2)(SO_4)_6Fe_2$, H_2SO_4, and may be represented by



$$\mathrm{SO_4H-Al_2}\left\{\begin{matrix}/\mathrm{SO_4}\backslash\\ /\mathrm{SO_4}\backslash\\ -\mathrm{SO_4}-\\ \backslash\mathrm{SO_4}/\\ \backslash\mathrm{SO_4}/\end{matrix}\right\}\mathrm{Fe_2-SO_4H}.$$

When heated, it is converted into the crystalline, colourless, neutral salt $(Al_2)(SO_4)_6(Fe_2)$.

The ferro-chromium compound $(Fe_2)(SO_4)_6(Cr_2)$ is also known. The acid compound $(Fe_2)(SO_4)_6(Cr_2)$, H_2SO_4 is crystalline, yellow, and insoluble.

The ferri-manganese compound $(Mn_2)(SO_4)_6(Fe_2)$ is crystalline, of a handsome green colour, and is decomposed by hydrochloric acid, chlorine being liberated.

49. **Ferric Selenide** (Fe_2S_3) is obtained by passing selenium vapour over red-hot iron, and fusing the product with an excess of

selenium and borax. This body has a metallic appearance, the sp. gr. is 6·38; it is fusible, and decomposes in air.

50. **Selenites of Iron.**—*A.* FERROUS SELENITE.—The method of preparation is by double decomposition.

The product forms a white precipitate, turning grey and afterwards yellow when left exposed to the air.

B. FERRIC SELENITE, $(SeO_3)_3(Fe_2)$, is a white powder (yellow after desiccation) obtained by double decomposition (Muspratt). When heated it parts with water, and at a higher temperature selenious anhydride is driven off, Fe_2O_3 being left.

When iron is dissolved in an excess of selenious acid in presence of HNO_3 a liquid is obtained which crystallises, on cooling, in small, pistachio-green lamellæ, consisting of $(SeO_3)_3Fe_2$, $3SeO_2$.

On treating these salts with ammonia a yellow basic salt, which passes through filter paper, is obtained.

51. **Seleniates of Iron.**—*A.* FERROUS SELENIATE (SeO_4Fe, $7H_2O$).—This salt is prepared by dissolving iron in dilute selenic acid, hydrogen being liberated and a compound left which at 0° crystallises like ferrous sulphate. At a higher temperature it crystallises like copper sulphate. It readily parts with its water, and becomes opaque.

B. FERRIC SELENIATE, $(SeO_4)_3Fe_2$, is prepared by double decomposition. It resembles ferric sulphate, and, like the latter, furnishes basic salts.

52. **Tellurites of Iron.**—*A.* FERROUS TELLURITE.—Light flakes, yellowish-grey in colour, obtained by double decomposition.

B. FERRIC TELLURITE.—Pale yellow precipitate of low stability, soluble in an excess of ferric salt.

54. **Nitrides of Iron.**—Iron and nitrogen combine with difficulty. On exposure at red heat to the action of gaseous ammonia, iron becomes white and brittle, and increases in weight by 12 to 13 per cent., which corresponds to Fe_4N_2.

The best method of preparing iron nitride is by acting with dry ammonia gas on anhydrous ferrous chloride heated to dark redness in a porcelain tube. NH_4Cl is liberated, a substance which is decomposed by water into Fe_2O_3, and NH_3 sublimes, and there remains in the tube a lustrous grey swollen mass endowed with the same properties as the nitride prepared from Fe and NH_3.

According to Rogstadius, when iron, reduced from the oxalate, is carefully heated in ammonia gas, there results a dull black mass which contains Fe_3N_2, and which, when strongly heated, gives off nitrogen and changes to Fe_6N_2.

When reduced to powder, iron nitride burns readily. On calcination it gradually parts with its nitrogen, the final traces being, however, difficult to eliminate. When heated in a current of hydrogen it yields iron and ammonia; and at red heat, in a current of steam, forms ferric oxide and ammonia. HCl and H_2SO_4 dissolve the nitride, hydrogen being given off and a ferrous salt formed together with an ammoniacal salt.

55. **Nitrates of Iron.**—*A.* FERROUS NITRATE, $(NO_3)_2Fe''$.—This salt is prepared either by dissolving ferrous sulphide in cold dilute nitric acid, or by double decomposition between barium nitrate and ferrous sulphate, ferric nitrate being formed, together with ammonium nitrate, when iron is dissolved in dilute nitric acid.

On evaporating neutral solutions of this salt at a low temperature it forms crystals with $6H_2O$. It is a greenish salt of low stability, dissolves in $\frac{1}{2}$ part of water at 0° and in $\frac{1}{3}$ part at 25° C., the latter solution having a density = 1·50. When boiled, ferrous nitrate is converted into insoluble ferric nitrate, the decomposition being facilitated by the presence of an acid.

B. FERRIC NITRATES.—I. *Normal Ferric Nitrate* $(NO_3)_6(Fe_2)^{VI}$.—The method of preparation is by dissolving ferric hydrate in HNO_3, or by attacking iron with nitric acid of sp. gr. 1·15. With weaker acid only ferrous nitrate or a mixture of ferrous-, ferric-, and ammonium nitrates would be formed. The liquid obtained by using acid of sp. gr. 1·115 is brown, and crystallises with difficulty in consequence of the presence of a basic nitrate. It is preferable, in order to obtain the crystallised nitrate, to take an acid of sp. gr. 1·332, and dissolve iron therein until the density reaches 1·5; by this means colourless limpid crystals are obtained on cooling. An excess of iron must be avoided, or the product will consist of basic nitrates instead of the normal salt.

Normal ferric nitrate forms several hydrates, the most common being that containing $18H_2O$, and separating out as clinorhombic crystals when a concentrated solution is slowly evaporated or cooled down. According to Ordway, the solution should be an acid one, containing 3 molecules of water to 2 of HNO_3.

With a solution containing $(NO_3)_6Fe_2$ per $2(HNO_3 + H_2O)$, crystals with $12H_2O$ are obtained, this hydrate being, according to Scheurer-Kestner, always formed when the solution is evaporated on the water bath, an operation resulting in supersaturation. On cooling below zero C., a crystalline mass containing $2H_2O$ is obtained, the mother liquor of which deposits crystals with $12H_2O$.

Ordway observed a hydrate with $6H_2O$, but this lacks further confirmation.

Commercial ferric nitrate, employed as a mordant in dyeing, also deposits crystals with $12H_2O$ when concentrated to 50° B.

The nitrate containing $18H_2O$ melts at 47·2°, and boils, with decomposition, at 125° C.; sp. gr. in the crystalline state, 1·6835, that of the melted salt being 1·6712. When mixed with sodium sulphate and dissolved in water the temperature of the solvent is reduced.

The following table gives the density of solutions of ferric nitrate of different strength, measured at 17·5° C. (Franz):—

Density.	$(NO_3)_6Fe_2$.	Density.	$(NO_3)_6Fe_2$.
1·0100	2 per cent.	1·3054	34 per cent.
1·0320	4 ,,	1·3286	36 ,,
1·0472	6 ,,	1·3512	38 ,,
1·0620	8 ,,	1·3746	40 ,,
1·0770	10 ,,	1·3982	42 ,,
1·0934	12 ,,	1·4218	44 ,,
1·1098	14 ,,	1·4465	46 ,,
1·1268	16 ,,	1·4719	48 ,,
1·1440	18 ,,	1·4972	50 ,,
1·1612	20 ,,	1·5272	52 ,,
1·1812	22 ,,	1·5572	54 ,,
1·2012	24 ,,	1·5892	56 ,,
1·2212	26 ,,	1·6232	58 ,,
1·2416	28 ,,	1·6572	60 ,,
1·2622	30 ,,	1·6956	62 ,,
1·2838	32 ,,	1·7340	64 ,,

II. *Basic Nitrates.*—Various basic nitrates are obtainable by dialysis, but their composition varies with the duration of the operation.

When a saturated solution of iron in nitric acid is prepared, basic salts are always produced, and to obtain the normal salt the proportions should be regulated according to the equation

$$8HNO_3 + 2Fe = (NO_3)_6Fe_2 + 2NO + 4H_2O.$$

The basic nitrates cannot be crystallised, and, moreover, their presence prevents the normal salt from crystallising.

When normal ferric nitrate is treated with sodium carbonate, or employed to dissolve ferric hydrate, a nitrate is obtained which is soluble in water and alcohol, may be precipitated by nitric acid, and corresponds to the formula

$$Fe_2O_3, 2N_2O_5 = 2[(NO_3)_6(Fe_2)], Fe_2O_3.$$

On dissolving ferric hydrate in the normal nitrate, in any desired proportion, the salt

$$Fe_2O_3, N_2O_5 = (NO_3)_6(Fe_2), 2Fe_2O_3 = (NO_4)_2(Fe_2)^{VI}$$

is obtained, representing the orthonitrate, derived from orthonitric acid $(NO_4)'''H$, corresponding to phosphoric acid $(PO_4)'''H_3$.

The action of boiling water on these nitrates, or on the normal salt, results in the formation of

(1) $2Fe_2O_3, N_2O_5 + H_2O = (NO_3)_6(Fe_2), 5Fe_2O_3 + 3H_2O$,

(2) $3Fe_2O_3, N_2O_5 + 2H_2O = (NO_3)_6(Fe_2), 8Fe_2O_3 + 6H_2O$,

(3) $4Fe_2O_3, N_2O_5 + 3H_2O = (NO_3)_6(Fe_2), 11Fe_2O_3 + 9H_2O$.

These nitrates are ill defined and uncrystallisable, and their method of preparation in itself indicates that a whole series of analogous bodies of variable composition can be obtained.

When solutions of ferric nitrate are boiled, they part with nitric acid and deposit a more highly basic nitrate.

If the elimination of nitric acid be prevented by heating the liquid in a sealed tube, the colour changes to brick-red, and a modified hydrate can be precipitated. A similar result is brought about by the action of light.

56. **Phosphides of Iron.**—A number of these have been described, but, according to C. Freese, the only ones that can be regarded as definite compounds are Fe_3P_4, Fe_2P_2, and Fe_4P_2.

All these phosphides are soluble in nitrohydrochloric acid, and nitric acid, with liberation of phosphoric acid. Dilute hydrochloric and sulphuric acids dissolve them but slowly, phosphoretted hydrogen being formed. They are only slightly fusible, and when heated in the air are converted into the corresponding phosphates, except in the case of Fe_3P_4, which commences by giving off phosphorus.

57. **Phosphites of Iron.** — *A.* FERROUS PHOSPHITE ($FeHPO_3$). — This salt is prepared by precipitating ferrous sulphate with phosphorus trichloride, neutralising the liquid with ammonia, washing the precipitate with boiling water, and drying *in vacuo*. It is readily oxidised, and decomposes, when heated, with incandescence and evolution of hydrogen.

B. FERRIC PHOSPHITE, $(Fe_2)H_3(PO_3)_3$, is prepared by treating ferri-ammonium sulphate with a mixture of ammonia and phosphorus trichloride. The white precipitate first formed is re-dissolved, but finally reappears; it should be washed with cold water and dried *in vacuo*. It contains $9H_2O$, and, when heated, decomposes, with emission of light.

58. **Hypophosphites of Iron.**—*A.* FERROUS HYPOPHOSPHITE.—Prepared by dissolving iron in pyrophosphorous acid out of contact with air. On evaporation *in vacuo* the solution deposits a crystalline mass containing $FeH_4(PO_2)_2$.

B. FERRIC HYPOPHOSPHITE, $(Fe_2)H_{12}(PO_2)_6$, prepared by dissolving ferric hydrate in cold hypophosphorous acid, is a white salt only sparingly soluble.

59. **Phosphates of Iron.**—*A.* FERROUS PHOSPHATES.—I. *Phosphate.*—$Fe_3(PO_4)_2$ is derived from orthophosphoric acid, H_3PO_4, and is obtained as a voluminous, white, gelatinous precipitate on adding sodium phosphate, drop by drop, to a ferrous salt.

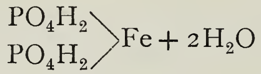
It oxidises rapidly, and turns blue in so doing. It may be prepared, containing 1 molecule of water, by the action of water at 50° C. on di-ferrous phosphate, and in this condition forms small dark green crystalline grains.

This phosphate is insoluble in pure water, but soluble in acidified water, and slightly so in water charged with carbon dioxide.

In nature it is known under the names of vivianite, triplite, etc.

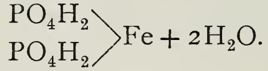
The phosphate $FeHPO_4$ is obtained, as a semitranslucent white powder, by the imperfect precipitation of ferrous sulphate by disodic phosphate, or boiling together phosphoric acid and iron. In the latter case the precipitate consists of small colourless needles, which turn blue in air and contain $FeHPO_4 + H_2O$.

Erlenmayer obtained the phosphate



$$\left.\begin{matrix}PO_4H_2\\PO_4H_2\end{matrix}\right\rangle Fe + 2H_2O$$

by dissolving iron in 48 per cent. phosphoric acid. It forms a green solution, which on addition of water deposits a white amorphous precipitate. When the solution is concentrated in an atmosphere of hydrogen there separates out a crystalline incrustation, which, on being washed with ether, resolves into a crystalline white powder of the formula



$$\left.\begin{matrix}PO_4H_2\\PO_4H_2\end{matrix}\right\rangle Fe + 2H_2O.$$

II. *Ferrous Pyrophosphate* (P_2O_7, Fe''_2).—This salt is derived from pyrophosphoric acid, P_2O_7, H_4.

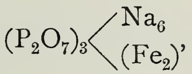
Sodium pyrophosphate gives with ferrous salts a white precipitate which changes in air, is insoluble in water, but soluble in dilute acids, ammonia, or in an excess of the ferrous salt or of an alkali pyrophosphate.

On agitating a mixture of ferrous sulphate and sodium phosphate with ammonia, a flocculent precipitate of ammoniacal pyrophosphate is formed, changing into crystalline flakes which are white when dried *in vacuo*. If a ferrous salt, saturated with nitrogen dioxide, be treated with sodium phosphate a brown precipitate of ferrous nitropyrophosphate, $P_2O_7Fe_2 + NO$, is formed. This precipitate absorbs oxygen from the air and turns white, being converted into a mixture of ferric phosphate and ferric nitrate.

B. FERRIC PHOSPHATES.—I. *Phosphate*, $(PO_4)_2(Fe_2) + 4H_2O$ (ferric orthophosphate), is obtained by precipitating a solution of ferric chloride by ordinary sodium phosphate. This precipitated phosphate is soluble in HCl, HNO_3, citric acid, or tartaric acid, but insoluble in sodium phosphate or phosphoric acid. It readily dissolves in water charged with carbon dioxide.

II. *Phosphate*, $(P_2O_7)_3(Fe_2)_2$ (ferric pyrophosphate), is obtained in precipitating sodium pyrophosphate with ferric chloride. The precipitate is soluble in sodium pyrophosphate, provided the ratio $Fe_2Cl_6 : 3P_2O_7Na_2$ has not been attained; but when the proportion $2Fe_2Cl_6 : 3P_2O_7, Na_2$ is reached, precipitation is complete and the solution no longer contains iron. The precipitate is soluble in a large excess of Fe_2Cl_6.

The above data indicate the existence of a sodium ferric salt

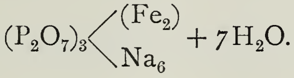


$$(P_2O_7)_3\left<\begin{matrix}Na_6\\(Fe_2)\end{matrix}\right.,$$

and ferric pyrophosphate $(P_2O_7)_3 (Fe_2)_2$. This double salt, however, has not been isolated.

Ferric pyrophosphate is soluble in acids, but the solution is re-precipitated by boiling. The precipitate has the same composition as the original salt, but is no longer soluble in dilute acids, though soluble in ammonia.

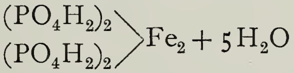
Ferric pyrophosphate is used in medicine, the phosphate of the German Pharmacopeia containing 1 or 2 molecules of sodium pyrophosphate in excess, and having the presumptive formula



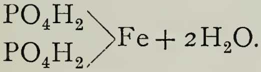
$$(P_2O_7)_3\left<\begin{matrix}(Fe_2)\\Na_6\end{matrix}\right. + 7H_2O.$$

Rieckher prepared the corresponding ammoniacal salt, containing $10H_2O$.

C. VARIOUS FERRIC PHOSPHATES.—I. *Phosphate* $(PO_4H)_3 (Fe)_2 + 2\frac{1}{2}H_2O$ (ferric triphosphate).—This salt was mentioned by Rammelsberg, who obtained it in the form of cubic crystals by leaving a saturated solution of the normal salt in an excess of acid for a year. Millot prepares it by dissolving ferric oxide in an excess of phosphoric acid, diluting with water and boiling. The crystalline white precipitate re-dissolves slowly in the mother liquor on cooling. The calcined salt is insoluble in acids.



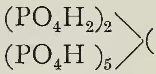
II. *Phosphate,* $\left.\begin{matrix}(PO_4H_2)_2\\(PO_4H_2)_2\end{matrix}\right>Fe_2 + 5H_2O$ (ferric tetraphosphate), is formed by the action of air on the acid ferrous phosphate,



$$\left.\begin{matrix}PO_4H_2\\PO_4H_2\end{matrix}\right>Fe + 2H_2O.$$

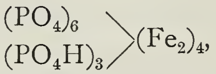
It was obtained by Erlenmayer, as bright red quadratic crystals, by the spontaneous evaporation of triferric phosphate in an excess of phosphoric acid. These crystals are unaltered by air and insoluble in cold water, but are decomposed by boiling water into phosphoric acid and triferric phosphate.

Millot prepares this salt by dissolving ferric hydroxide in phosphoric acid.

Erlenmayer obtained the salt  $\left.\begin{matrix}(PO_4H_2)_2\\(PO_4H\ )_5\end{matrix}\right\rangle(Fe_2)_2$, as a rose-red crystalline powder, by concentrating a solution of acid ferrous phosphate in the air.

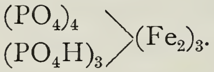
III. *Phosphate* $(PO_4H_2)_6(Fe_2)$ (ferric hexaphosphate).—To prepare this phosphate, ferric hydroxide is added to a 48 per cent. solution of phosphoric acid until a white deposit is produced; the solution then contains $14PO_4H_3$ per Fe_2O_3. On evaporating it on the water bath there is formed a crystalline incrustation, which, when washed with ether, yields a rose-red crystalline powder that decomposes, on exposure to air, into phosphoric acid and a less acid phosphate, $2P_2O_5$, Fe_2O_3, $8H_2O$.

Cold water converts ferric hexaphosphate into a nearly neutral phosphate,



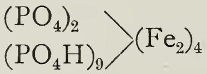
$$\left.\begin{matrix}(PO_4)_6\\(PO_4H)_3\end{matrix}\right\rangle(Fe_2)_4,$$

which is also obtained when the above-mentioned solution, containing $14PO_4H_3$ per Fe_2O_3, is poured into 21 times its own volume of boiling water. With cold water the same solution furnishes a yellowish-grey precipitate containing



$$\left.\begin{matrix}(PO_4)_4\\(PO_4H)_3\end{matrix}\right\rangle(Fe_2)_3.$$

With alcohol the salt



$$\left.\begin{matrix}(PO_4)_2\\(PO_4H)_9\end{matrix}\right\rangle(Fe_2)_4$$

is obtained.

Boiling water decomposes all these salts in converting them into forms more and more approximating to the normal phosphate $(PO_4)_2(Fe_2)$.

IV. *Basic Ferric Phosphates.*—On precipitating acid solutions of the foregoing acid phosphates by ammonia there results the basic phosphate $2(PO_4)_2(Fe_2), Fe_2O_3 + 8H_2O$, which is characterised by its insolubility in ammonium citrate and solubility in ammonium oxalate.

If ammonia be added to the acid solution of this basic salt the phosphate $(PO_4)_2(Fe_2)$, Fe_2O_3 is obtained; this is only sparingly soluble in ammonium citrate or oxalate.

A natural basic phosphate, occurring as a brown mass with the composition $(PO_4)_2(Fe_2)$, $Fe_2O_3 + 12$ or $24H_2O$, is met with at Bernau (France) and in Mauritius.

60. **Arsenides of Iron.** — Arsenic combines with iron in several proportions, forming bodies harder, more brittle, and more fusible than iron itself. When heated, the arsenides of iron yield an arsenical sublimate; and, when roasted in the air, furnish arsenious anhydride and a magnetic residue. They are soluble in nitric acid and in *aqua regia.*

61. **Arsenites of Iron.**—*A.* FERROUS ARSENITE (FeH, AsO_3).—This is a white precipitate, soluble in NH_3, oxidising rapidly in air to an ochreous yellow substance, and is prepared by treating ferrous sulphate with ammonium arsenite. When calcined it parts with water and arsenious anhydride, a rust-coloured residue being left.

B. FERRIC ARSENITE $(Fe_2)^{VI}(AsO_3)_2$. — Potassium arsenite gives with Fe_2Cl_6 a rust-coloured precipitate consisting of an arsenite more basic than the normal salt. The same basic salt is formed on digesting ferric hydroxide with arsenious anhydride and water; and the insolubility of this compound explains the action of *freshly prepared* ferric hydroxide as an antidote for arsenious acid poisoning.

62. **Arsenates of Iron.**—*A.* FERROUS ARSENATE ($FeHAsO_4$). —This is obtained, as a white precipitate, on treating ferrous sulphate by ammonium arsenate. It rapidly turns a dirty green colour in changing into ferro-ferric arsenate. When heated it loses arsenious acid, and leaves a residue of ferric oxide and ferric arsenate. It is sparingly soluble in NH_3.

B. FERRIC ARSENATES.—The neutral arsenate $(AsO_4)_2(Fe_2)^{VI}$

is obtained on oxidising the ferrous salt by nitric acid and precipitating the solution by ammonia.

This arsenate when heated to redness becomes suddenly incandescent. Only a portion of the arsenic acid in this salt can be removed by caustic potash; and in order to effect complete decomposition, digestion with ammonium sulphide is necessary.

The acid arsenate $(Fe_2)^{vi}H_3(AsO_4)_3 + 4\frac{1}{2}H_2O$ is a white powder insoluble in water. When heated it parts with water, becomes red, and subsequently yellow, by changing into pyro-arsenate, $(Fe_2)_2(As_2O_7)_3$.

Several ferric arsenates are met with in nature, among them being—

Eisensister: $(Fe_2)^{vi}(AsO_4)_2 + Fe_2H_6O_6 + 9H_2O$;
Scorodite: $(Fe_2)^{vi}(AsO_2)^2 + 4H_2O$;
Wurfelerz: $(Fe'')_3(AsO_4)_2 + 2[(Fe_2)^{vi}(AsO_4)_2] + 4(Fe_2)^{vi}H_6O_6 + 18H_2O$.

63. **Sulpharsenites of Iron.**—*A.* FERROUS PYROSULPHARSENITE $(Fe''_2As_2S_5)$.—This is a blackish-brown precipitate dissolving to a yellow solution in an excess of alkali sulpharsenite. When heated it parts with arsenic, a residue of ferrous sulphide being left.

B. FERROUS SULPHARSENITE.—An olive-green precipitate soluble in an excess of the precipitant, fusible, and decomposed at red heat, leaving behind a residue of ferrous sulphide. Berzelius gives it the formula $Fe_2S_3(As_2S_3)_5$.

64. **Sulpharsenates of Iron.**—*A.* FERROUS PYROSULPHARSENATE $(As_2S_7)Fe''_2$.—A dark brown precipitate, soluble in an excess of the precipitating reagent. It decomposes on desiccation.

B. NORMAL FERRIC SULPHARSENATE $(Fe_2)^{vi}(AsS_4)_2$.—A greenish-grey, flocculent precipitate, readily soluble in an excess of alkali sulpharsenate.

65. **Carbides of Iron.**—In a state of fusion iron combines direct with carbon, forming a series of carbides. When the carbon is in excess it dissolves in the molten metal, but a portion separates out, on cooling, in the form of crystallised graphite, which remains embedded in the metallic mass.

The carbide Fe_3C (cementite, normal carbide, carbide of white cast iron, cementation carbide) is the only definite iron carbide known (H. le Chatelier, *Revue générale des Sciences*, Jan. 15, 1897). Owing to its tendency to split up at high temperatures into iron and graphite, it cannot be prepared by fusing the metal in presence of carbon. Marguerite obtained it by heating finely divided ferric oxide to incipient redness in carbon monoxide. Abel, Müller, and Arnold, by treating tempered steel and white cast iron with suitable reagents, extracted metallic scales of a very high degree of hardness, corresponding to the formula Fe_3C.

The calcination of ferrocyanides furnishes a carbide containing C_2Fe in the form of a readily ignitible black powder.

Prussian blue yields on calcination another carbide corresponding to C_3Fe_2.

The different grades of cast iron and steel are nothing more than iron carbides of variable composition.

66. **Carbonates of Iron.**—*A*. FERROUS CARBONATE ($FeCO_3$). —Metallic iron is gradually dissolved by water charged with carbon dioxide, ferrous carbonate being formed. By passing a current of CO_2 for several hours through water containing in suspension iron reduced by hydrogen, a solution of ferrous carbonate (0·91 grm. per litre) is obtained.

Hydrated $FeCO_3$ is obtained by double decomposition, as a voluminous white precipitate which oxidises and turns brown in the air. It is insoluble in water, but dissolves, as a bicarbonate, in water charged with CO_2. This solubility varies inversely with the temperature, the saturated solution containing 1·39 grms. of ferrous carbonate per litre at 15° C.; whilst at 24° C. not more than 0·098 grm. is present. On driving off all the CO_2 the whole of the $FeCO_3$ is precipitated. It is also thrown down by alkali carbonates, though the bicarbonates have no such action. Chlorides and sulphates appear to impart stability to the solution.

Ferrous carbonate is met with, in nature, in a crystalline or amorphous state (siderose, spathic iron), and forms one of the best ores of iron. When calcined it gives off carbon monoxide and carbon dioxide, a residue of intermediate magnetic oxide being left.

B. Ferric Carbonate.—The normal salt has not been isolated, attempts to prepare it by double decomposition resulting in the production of the hydrate containing more or less CO_2.

Alkali bicarbonates dissolve ferric hydroxide to a red solution, precipitable by boiling, and from which ferric hydroxide is separated by alkalis.

67. **Sulphocarbonates of Iron.**—*A*. Ferrous Sulphocarbonate ($FeCS_3$).—When an alkali sulphocarbonate is added to ferrous sulphate a red liquid, gradually becoming almost black, is obtained. An excess of sulphocarbonate deepens the colour of the solution, whilst an excess of the ferrous salt throws down the compound in the state of a black powder.

B. Ferric Sulphocarbonate is a dark brown precipitate collecting in granules insoluble in water. Under the influence of heat it parts with sulphur and carbon disulphide, ferrous sulphide being left.

68. **Iron Nitrosulphocarbonate** ($Fe_4S(NO)_6, CS_2 + 3H_2O$).—This body is related to the nitrosulphides of Roussin. It was discovered by O. Lœw, and is prepared by gradually adding and stirring a mixture of dissolved sodium sulphocarbonate and nitrite to a solution of ferrous sulphate, the whole being then raised to boiling and filtered. On cooling, black needles are obtained, which are purified by re-crystallising in water and ether, and correspond to the formula $Fe_4S(NO)_6, CS_2, 3H_2O$. These crystals are soluble in water, alcohol, ether, etc. The aqueous solution is black, and yields up its salt to ether. When kept for some time the crystals lose water and nitrogen dioxide.

Acids and alkalis have little effect on the solution in the cold; but in the warm, alkalis liberate ammonia and precipitate ferric hydroxide, a new class of alkali salts being formed at the same time.

Potassium cyanide converts iron nitrosulphocarbonate into alkali nitrocyanide. O. Lœw regards this nitrosulphocarbonate as the nitro-derivative of a hypothetical sulphocarbonate, $Fe_4S_4CS_2$.

69. **Silicates of Iron.**—Normal ferrous silicate (SiO_4Fe_2) is formed during the refining of cast iron. It is very fusible, and

susceptible to attack by acids, and occurs either in amorphous masses or as grey crystals of metallic aspect.

When a crystal of ferrous sulphate is introduced into a solution of potassium silicate, partially carbonated, it becomes covered with a grey vegetation (tree of Mars), which contains basic ferrous silicate and potassium carbonate in the proportion of $2K_2CO_3$ to $3Fe''_2SiO_4$, $6FeO$. This product is insoluble in water; on exposure to the air it oxidises and is transformed into ferric silicate $(Fe_2)_2(SiO_4)_3 + 4Fe_2O_3$.

Silicates of iron are abundant in nature.

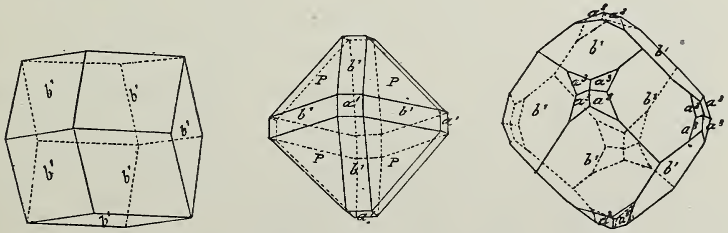
70. **Iron Boride** is obtained on reducing the borate by hydrogen. It is a hard white body dissolving in acids to form boric acid and a ferrous salt, hydrogen being liberated. Boiling water decomposes it into boric acid and iron.

71. **Borates of Iron.**—*A.* FERROUS BORATE.—This is obtained by double decomposition, and appears to correspond to the formula BO_2Fe, but loses boric acid when washed.

B. FERRIC BORATE.—This salt forms an insoluble yellow powder, turning brown on calcination and vitrifying at a bright red heat.

§ 3. IRON ORES

72. **Anhydrous Oxides.**—*A.* FERRO-FERRIC OXIDE.—I. *Magnetic Oxide* (magnetite) (Fe_3O_4) consists of ferro-ferric oxide, frequently associated with small quantities of titanium, manganese, and magnesium.



FIGS. 36, 37, and 38.—Ferro-ferric oxide.

Magnetite occurs as isolated crystals or in granular masses, lamellar or compact, or as rounded grains. It is of a dark iron-grey colour, lighter in the case of the crystals, which have a brighter lustre. The powder is black.

This oxide is found almost exclusively in the crystalline metamorphic rocks; frequently in considerable masses, as at Taberg in Sweden, and Blagodat in the Ural, where it forms veritable mountains.

It is extensively mined, and forms the best iron ore for high-class steel. It occurs disseminated in the form of small grains in many schistous rocks and in the majority of the eruptive rocks. The finest specimens of crystals are obtained at Traverselle in Piedmont, and at Normark in Wermeland.

Magnetite is soluble in HCl. It fuses with difficulty before the blowpipe; in the oxidising flame it loses its magnetic properties; with fluxes it gives the reactions for iron.

Magnetite will scratch fluor spar, but is itself scratched by quartz. The degree of hardness is 5·5 to 6; sp. gr., 5 to 5·2. It is highly magnetic, and crystallises in the cubic system, regular octahedra being the most general form, though sometimes it occurs as rhomboidal dodecahedra or a combination of these two forms with the icositetrahedron, the trioctahedron. The cube facets are rare.

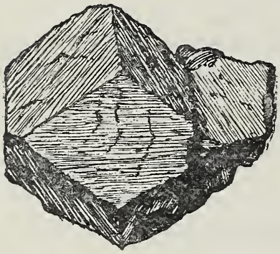


FIG. 39.—Magnetite.

B. FERRIC OXIDE.—I. *Haematite* (syn.: Specular iron, red oxide, oligistic iron) (Fe_2O_3) is most frequently met with as crystals, or lamellar or scaly masses. The colour is steel-grey with a metallic lustre, and the crystals have an iridescent surface. In thin plates it is translucent, and the powder is red.

Hæmatite is one of the most abundant minerals. The crystalline variety belongs principally to the crystalline rocks, where it is found in veins or in masses, associated with quartz, in Sweden, Norway, the Ural Mountains, on the island of Elba, etc. In Brazil it constitutes a true rock (itabirite) formed of a mixture of hæmatite and quartz. In the volcanic rocks it is met with as lustrous plates.

The compact and fibrous varieties form deposits at the contact of gneiss or granite with liassic or other limestones. They are found in certain strata of primary or secondary rocks, such as the red sandstones, Vosgian sandstones, etc. This oxide also enters into the composition of ochre.

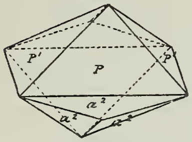


Fig. 40.—Oligistic iron (hæmatite). (Primitive basal form.)

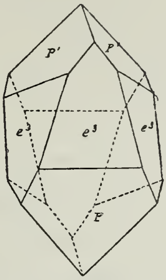


Fig. 41.—Oligistic iron (hæmatite). (Primitive and rhombohedral.)

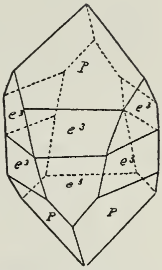


Fig. 42.—Oligistic iron (hæmatite). (From the Altenberg mines.)

The sp. gr. is 5·2 to 5·3; hardness, 5·5 to 6·5. It is soluble in boiling concentrated HCl, is infusible in the oxidising flame, and but slightly fusible in the reducing flame, in which it is converted into magnetite.

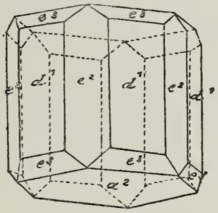


Fig. 43.—Hæmatite (Framont).

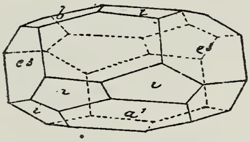


Fig. 44.—Hæmatite (St. Gothard).

The crystalline form is that of the rhombohedron (86° 10′), but is rarely met with unmodified.

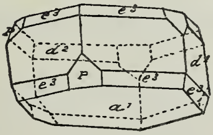


Fig. 45.—Hæmatite (Mont-Dore).

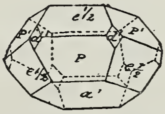


Fig. 46.—Hæmatite (Mont-Dore).

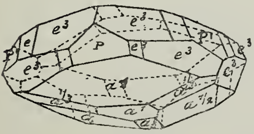


Fig. 47.—Hæmatite.

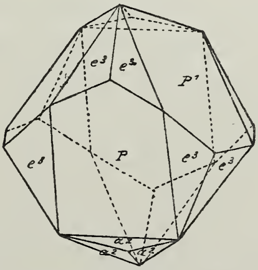


Fig. 48.—Hæmatite (Elba).

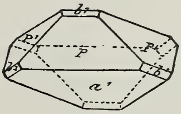


Fig. 49. — Hæmatite (primitive based by facets of the equiaxial rhombohedron).

The name of *martite* has been given to hæmatite, crystallised in octahedra and resulting from a pseudomorphosis of magnetite into hæmatite. Some mineralogists, however, have regarded hæmatite as actually dimorphous.

II. *Ilmenite* is composed of ferric oxide (Fe_2O_3), in which a portion of the Fe is replaced by Ti. It occurs in rhombohedral crystals resembling those of hæmatite; frequently also in lamellæ flattened parallel to the base; and sometimes in very pointed rhombohedra, iron-black in colour and of faintly metallic lustre. The fracture is plain.

Ilmenite is found in granite rocks, sands, etc. It is soluble with difficulty in HCl, and the solution turns blue when boiled with tin. With sodium, ammonium phosphate, and tin, in a reducing flame, it gives the violet coloration of titanium.

Hardness, 5 to 6; sp. gr., 4·5 to 5.

FIG. 50.
Ilmenite.

73. **Hydrated Oxides.**—*A.* LIMONITE, or brown hæmatite, is a natural ferric hydroxide ($2Fe_2O_3, 3H_2O$), and an extremely abundant ore of great importance. It occurs as *fibrous limonite*, in kidney-shaped concretions, or in masses with a lustrous black surface, or again in compact dark brown masses, of plain fracture, as veins in the older rocks and in contact deposits (Pyrenees, Isère, etc.).

The pisolitic ore is found in globules, with a compact fracture, disseminated in the clays of the middle tertiary deposits, or cemented by an argilo-calcareous paste. Such deposits frequently cover the plateau of Jurassic limestone or chalk; they are common in the districts of Berry, the Bourbonnais, Lorraine, Franche-Comté, etc.

The oolitic ore is found in smaller grains than the preceding variety. These grains, often agglomerated together, form rocks that for the most part are situated at the base of the oolitic limestones. This ore contains fossils, and is of lower value than the pisolitic variety. It is worked in the departments of Gard, Ardèche, Aveyron, Côte-d'Or, Jura, Haute-Marne, etc.

Earthy Limonite has a smooth fracture, and is often highly argillaceous. It is found in various secondary and tertiary rocks.

Bog Ore contains a large proportion of phosphorus, and furnishes a phosphoric cast iron.

Limonite is soluble in acids, and frequently leaves a siliceous residue. Heated in a tube it gives off water. The dust is yellowish brown. Hardness, 5 to 5·5; sp. gr., 3·6 to 4.

The following table gives the results of analyses performed on several varieties of limonite:—

Constituents.	Hæmatite from Vicdessos.	Granular Hæmatite from Mt. Girard, near St. Dizier.	Granular Ore from Eurville (Hte.-Marne).	Granular Ore from Bruères (Niévre).	Oolitic Ore from Mondalazac (Aveyron).	Oolitic Ore from Vellesprey (Hte.-Saône).
Fe_2O_3 . . .	82·00	69·00	58·20	46·40	48·60	37·00
Mn_2O_3 . . .	2·00	...	...	...	0·35	1·40
Water . . .	14·00	16·00	15·00	13·00	12·60	13·50
Silica . . .	1·00	...	...	...	...	...
Clay. . . .	...	14·20	26·80	40·00	12·41	37·20
Phosphoric acid .	...	...	...	...	0·21	0·22
Soluble alumina .	...	...	...	...	4·10	1·00
Calcium carbonate .	...	...	...	...	20·60	9·40
Magnesium carbonate	...	...	...	...	...	0·18

B. GŒTHITE (lepidocrocite, pyrrhosiderite).—This is a ferric hydroxide ($Fe_2O_4H_2$), occurring as longitudinally striated crystals, as crystalline lamellæ, in scales, or fibrous masses of a brown, yellow, or red colour. It is found along with other iron ores, but more particularly near Siegen and in Cornwall.

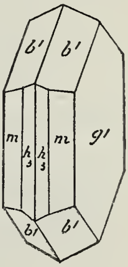


FIG. 51.
Gœthite.

The crystalline form is the orthorhombic prism, $mm = 94^\circ\ 52'$, $b^{1}/_{2}b^{1}/_{2} = 121^\circ\ 4'$, $b^{1}/_{2}b^{1}/_{2}$ in front $126^\circ\ 18'$. Cleavage, g' perfect.

C. TURGITE (hydrohæmatite) is another ferric hydroxide ($2Fe_2O_3$, H_2O), forming an abundant ore of iron, resembling limonite, but harder, and yielding a paler red powder. When heated in a tube it decrepitates and gives off water.

74. **Iron Spinels.**—*A.* FRANKLINITE is a spinel of iron, zinc, and manganese—

$$RR_2O_4;\ R = Fe, Zn, Mn;\ R_2 = Fe_2, Mn_2,$$

occurring in octahedral crystals or in granular or compact black masses, accompanying red zinc oxide in a crystalline limestone at Hanbury (New Jersey).

This body is soluble in HCl; it is infusible before the blowpipe. With borax it gives an amethyst-violet bead in the oxidising flame, and a bottle-green bead in the reducing flame.

The degree of hardness varies between 5·5 and 6·5, and the sp. gr. between 5·6 and 5·9. The powder is brownish red. The crystalline form is the regular octahedron, modified by facets of the rhomboidal dodecahedron.

75. **Sulphidic Ores.** — *A.* PYRRHOTINE (hepatic pyrites, magnetic pyrites) approximates in composition to Fe_7S_8. This sulphide is occasionally met with as very fine flattened hexagonal crystals; more frequently in lamellæ or compact masses with a faint metallic lustre, yellow or bronze, and conchoidal fracture. It occurs at Königsberg, Modum, Snarum (Norway), Andreasberg (Hartz), and Bodenmais (Bavaria). It frequently contains nickel, and then forms an important ore of that metal (Varelle, Piedmont, etc.). The finest specimens of crystals come from the gold mines of Moro-Velho (Brazil). Pseudomorphic forms are met with in pyrites, limonite, and siderose.

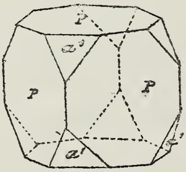


FIG. 52.—Magnetic pyrites.

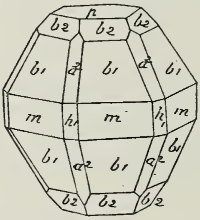


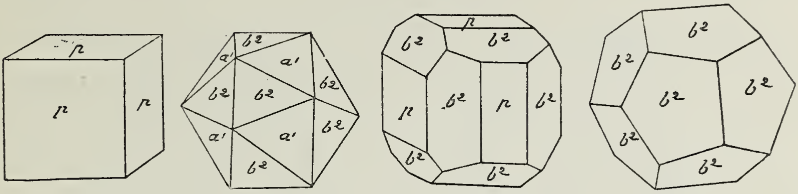
FIG. 53.—Pyrrhotine.

This mineral is soluble in acids. Heated in open tubes it gives off sulphur dioxide, and on charcoal it furnishes a black magnetic mass which, in presence of a flux, gives the reactions of cobalt and nickel.

The hardness is 3·5 to 4·5; the sp. gr., 4·4 to 4·7.

Magnetic pyrites crystallises in the form of a regular hexagonal prism, in which one of the sides of the base is nearly equal to the height. The crystals exhibit cleavages parallel to the 6 facets of the prism and one in the direction of the base, the latter being particularly definite.

B. TROÏLITE consists of ferrous sulphide in grains or nodules of various sizes cemented in meteoric iron. It exhibits an unequal fracture.



FIGS. 54 to 57.—Crystals of pyrites.

C. PYRITES (yellow sulphide of iron).—Pyrites consists of the iron sulphide FeS_2. It is nearly always crystalline, but is occasionally met with in concretion as compact, globular, stalactitic, granular, pseudomorphic masses, modelled on crystals of other substances or on fossils. The crystals are often very handsome, of a golden-yellow colour with a fine polish and a bright metallic lustre.

Pyrites is abundantly distributed throughout nearly all geological ages. Occasionally it has undergone modification into limonite. It is mined in considerable quantity at Chessy (near Lyons), etc., as a sulphur mineral and for sulphuric acid manufacture.

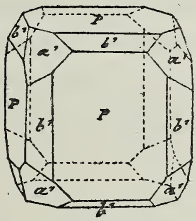


FIG. 58.—Cubo-dodecahedral pyrites.

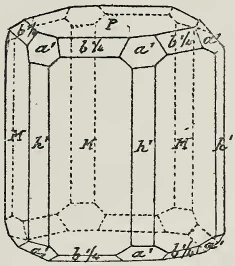
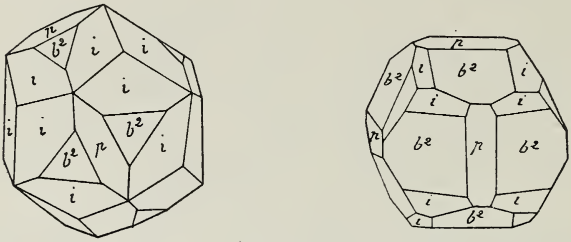


FIG. 59.—Pyrites from a Cumberland mine.

Pyrites is unacted upon by hydrochloric acid, but is dissolved by nitric acid, with separation of sulphur. When heated in a tube it yields sublimed sulphur and a magnetic residue, and on carbon it burns with a blue flame. It strikes fire with steel. The degree of hardness is 6 to 6·5 ; sp. gr., 4·8 to 5·2 ; fracture, unequal or conchoid ; texture, brittle. The powdered substance is of a greenish-grey colour.

The crystals of pyrites belong to the cubic system, but are affected by hemihedry with parallel facets. This hemihedry is generally manifested, even on the cubes, by striæ, which on each facet are parallel to two opposite sides of the face in such a manner as to be mutually perpendicular in three adjoining facets. In addition, the octahedron a^1 is frequently encountered, often modified by faces of the pentagonal dodecahedron b^2, and forming the icosahedron $a^1\frac{b^2}{2}$ when the forms equilibrate. The pentagonal dodecahedron b^2 is very frequent, as well as hemihexoctahedron with parallel faces (b^1, $b^1/_3$, $b^1/_2$), etc. The faces b^1, b^3, $b^5/_2$, $b^3/_2$, $b^4/_3$, $b^6/_5$ (the two latter frequently the reverse of the dodecahedron b^2), (b^1, $b^1/_5$, $b^1/_{10}$), (b^1, $b^1/_5$, $b^1/_8$), (b^1, $b^1/_3$, $b^1/_4$), etc., are also met with.

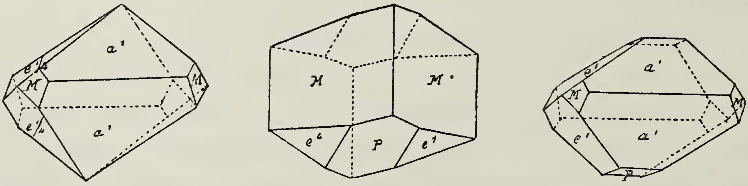


FIGS. 60 and 61.—Crystals of pyrites.

The cube is almost invariably the general form, despite the number of facets with which the crystals are often surcharged.

Groupings of crystals parallel to the faces of the cube or of the octahedron are also known; occasionally two crystals intersect each other in two rectangular positions.

D. MARCASSITE or white pyrites is composed, like the preceding variety, of FeS_2. It is yellowish or greenish-white in colour with a metallic lustre, and occurs as crystals in veins, or as balls or fibrous renal masses of radial structure disseminated in clays, marls, chalk, etc.;



FIGS. 62, 63, and 64.—White pyrites.

or again, in particles (often imperceptible) in schists, lignites, coal, etc. Its property of rapidly oxidising in air causes it to be worked in large quantities for the manufacture of ferrous sulphate or alum. The aluminous schists or lignites containing marcassite are attacked by the sulphur dioxide resulting from the decomposition of this sulphide and its conversion into ferrous sulphate.

This pyrites is also met with in imitative dendritic or pseudomorphic forms. It is insoluble in HCl, but attacked by HNO_3. Heated in a closed tube it furnishes a sublimate of sulphur. The hardness is 6 to 6·5 ; sp. gr., 4·6 to 4·8 ; fracture, unequal ; colour of the powdered substance, greenish grey.

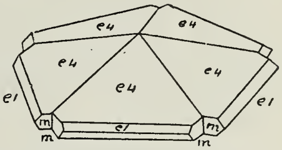


Fig. 65.—Marcassite. Grouping of crystals known as "crête de coq" (cockscomb).

The crystalline form is the orthorhombic prism, the most frequent shapes being prismatic or octahedral. The crystals are often macleated parallel to *m*, so as to form pentagonal lenticular masses.

E. Chalcopyrite (cupreous pyrites).—This is a sulphide of iron and copper (Cu_2S, Fe_2S_3), which forms one of the most abundant ores of the latter metal. It occurs in compact concretionary masses, or as octahedral or tetrahedral crystals, of a deep golden-yellow colour with an iridescent reflection ; in veins embedded in gneiss, argillaceous schists, etc. The crystalline form is the quadratic octahedron.

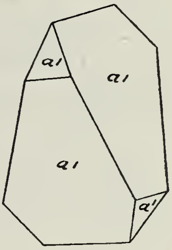


Fig. 66.
Chalcopyrite.

76. **Sulphatic Ores.**—*A.* Melanterite (green vitriol) consists of ferrous sulphate ($FeSO_4$, $7H_2O$). It occurs as clear crystals, or as fibrous or concretionary masses resulting from the decomposition of pyrites. It changes and turns brown on exposure to air. The hardness is 2 ; sp. gr., 1·8 to 2 ; and the crystalline form is the clinorhombic prism.

B. Fibro-ferrite (stypticite). — This is a hydrated ferric sub-sulphate ($3Fe_2O_3$, $5SO_3 + 27H_2O$), occurring as masses or fibrous bundles, translucent, pale yellow or greenish, and with a silky lustre.

It is insoluble in water. When heated in a tube it liberates water and (at a high temperature) sulphur dioxide and sulphur trioxide, leaving a residue of ferric oxide.

C. COPIAPITE is also a hydrated ferric sub-sulphate, $2Fe_2O_3, 5SO_3 + 18H_2O$, forming hexagonal, tabular, fibrous or yellow granular masses, and is found in the Copiapo copper mines (Chili).

D. COQUIMBITE is another hydrated ferric sulphate, of the formula $Fe_2O_3, 3SO_3 + 9H_2O$, and is a yellowish-white salt completely soluble in water. It crystallises in hexagonal tables, cleaving parallel to the base, or occurs in granular masses. The hexagonal prisms are frequently modified at the basal edges.

E. BOTRYOGENE (red vitriol).—A hydrated ferro-ferric sulphate containing magnesia and lime, and forming small crystals or botryoid masses, red to brown in colour, and found incrusting gypsum or pyrites in the mines of Fahlun.

This salt is partly soluble in water, leaving an ochreous residue. The hardness is 2 to 2·5; sp. gr., 2·04; crystalline form, the clinorhombic prism.

77. **Phosphatic Ores.**—*A.* VIVIANITE (phosphatic iron).—Vivianite is hydrated ferrous phosphate; formula, $(PO_4)_2Fe_3, 8H_2O$. It forms more or less elongated light blue prismatic crystals, frequently modified, and then presenting a blackish appearance. It is transparent, tender, and flexible.

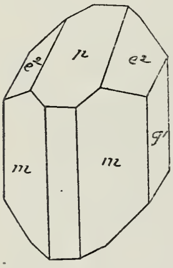


FIG. 67.—Vivianite.

Vivianite is often found associated with pyrrhotine and chalcopyte in the stanniferous veins of St. Agnes (Cornwall), in clay beds, and in the cavities of fossils (Crimea). It has been discovered in burned-out colliery workings (Cransac, Aveyron).

It is soluble in HCl; heated in a tube it gives off water, bleaches, and becomes exfoliated. Before the blowpipe it melts readily, and imparts a greenish-blue colour to the flame. The powder is bluish-white; hardness, 1·5 to 2; sp. gr., 2·5 to 2·7; crystalline form, the clinorhombic prism.

B. TRIPHYLLINE is a phosphate of manganese, iron, and lithium, RLiPO$_4$; R = Fe, Mn, with Mg, Ca, Na, etc. It is occasionally met with as large crystals, more often as cleavable masses, greenish grey or blackish in colour; it crystallises in orthorhombic prisms.

Nordenskiold has given the name tetraphylline to a mineral he discovered at Keild in Finland, and which possesses the same form and external characteristics as triphylline.

C. TRIPLITE. — This phosphate occurs in blackish brown imperfect lamellar masses, and cleaves in three apparently rectangular directions. It is a fluophosphate of iron and manganese, $PO_4R(R''F)'$; R = Mn, Fe, with traces of lime.

The lustre is greasy or resinous, the fracture subconchoidal. It is fragile, and gradually soluble in acids. The hardness is 4 to 5·5; sp. gr., 3·4 to 3·8. It has been found in pegmatite near Limoges, and at Peilau (Silesia).

D. DUFRENITE (Delvauxine). — This is a hydrated ferric phosphate, $PO_4[Fe_2, 3(OH)]''' = \frac{1}{2}[P_2O_5, 2Fe_2O_3, 3H_2O]$, and forms concretionary or fibrous masses dark green in colour, changing to yellow and brown when subjected to alteration. It is soluble in acids; the hardness is 3·5 to 4; the sp. gr., 3·2 to 3·4; the crystals are in the form of orthorhombic prisms.

E. CACOXENE.—This is a hydrated phosphate of iron and alumina, which occurs as ochre-yellow fibrous masses, with a faint metallic lustre and of ill-defined composition. Hardness, 2·3 to 3·3.

78. **Minerals containing Arsenic.**—*A.* MISPICKEL (arsenical pyrites, arsenopyrites).—The formula of this ore is $2FeAsS = FeS_2 + FeAs_2$. It forms elongated prismatic crystals or fibrous, compact, crystalline masses of a handsome silver-white colour, sometimes yellow on the surface, and with a bright metallic lustre.

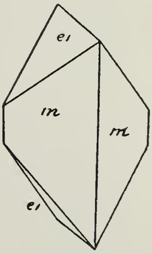


FIG. 68. Mispickel.

Mispickel is found principally in crystalline rocks associated with ores of tin and silver. Nitric acid attacks it and separates sulphur and arsenic acid. When heated in an open tube it yields a white sublimate of arsenious acid, whilst in sealed tubes it furnishes at first a red sublimate of arsenic sulphide and subsequently a black sublimate of metallic arsenic.

The degree of hardness ranges between 5·5 and 6; the sp. gr. from 6 to 6·4; the crystalline form is the orthorhombic prism, $mm = 111° 53'$; $e^1e^1 = 99° 52'$.

B. Iron Arsenate (pharmocosiderite) is a hydrated ferric arsenate containing a little phosphorus and copper: $2As_2O_5$, $3Fe_2O_3$, $12H_2O$.

This mineral, which is dark green (or occasionally brown) in colour, is always crystalline. It is also found in lustrous, translucent, granular masses (Cornwall, St. Léonard near Limoges, Horhausen in Nassau). In hardness it compares with carbonate of lime, and the sp. gr. is 2·9 to 3. It is soluble in HCl. Heated in a tube it turns red and gives off water; and before the blowpipe, on charcoal, arsenical fumes are evolved. The usual form of the crystals is the cube with tetrahedric hemihedry.

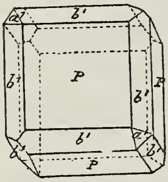
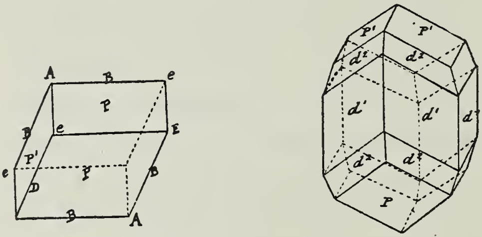


Fig. 69.
Pharmocosiderite.

79. **Iron Carbonate.**—*A.* Siderose (spathic iron) consists of ferrous carbonate ($FeCO_3$), containing in admixture variable quantities of $CaCO_3$, $MgCO_3$, $MnCO_3$, etc.

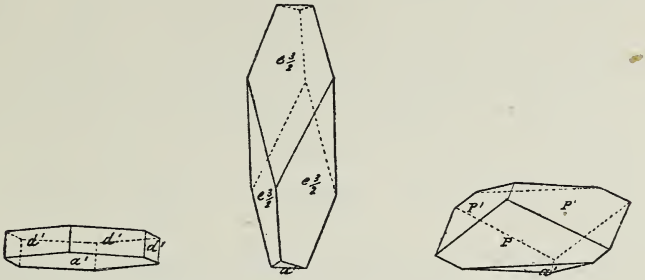
It sometimes occurs in darkish crystals, but more commonly as lamellar, granulated, amorphous, or renal masses.

The lamellar variety has received the name of *spathic iron*, and the amorphous kind is known as lithoid carbonate of iron.



Figs. 70 and 71.—Spathic iron.

Siderose is white in colour, inclining to pale yellow, but when altered assumes various shades—yellow, brown, or ochre red. Occasionally it is black (lithoid carbonate in colliery workings), and may be transparent, translucent, or opaque, the lustre being vitreous or tarnished, and the powder grey. It is met with in beds or veins in the older rocks, and forms a valuable iron ore. The lithoid variety is met with as continuous beds, or regularly deposited renal masses, in the coal measures; and the oolitic variety occurs in the sandstones and clays of the Secondary or Tertiary formation.



Figs. 72, 73, and 74.—Spathic iron.

Siderose is soluble in acids, with effervescence, gradual in the cold, very brisk when heat is applied. Before the blowpipe it blackens and runs together to form a magnetic mass. The hardness is 3·5 to 4·5; and the sp. gr., which fluctuates between 3·7 and 3·9, decreases to as low as 3 in the earthy varieties.

The primitive and most frequent crystalline form is an obtuse rhombohedron, $pp = 107$, with three easy cleavages parallel to the faces of the rhombohedron, which faces are often curved. The obtuse rhombohedron *b*, formed by tangential modifications on the edges, and termed "equiaxial," is as plentiful as the primitive form.

80. **Silicates of Iron** constitute an extremely numerous series in nature, principally, however, in combination with other silicates.

A. FAYALITE.—This mineral, obtained on the island of Fayal, is an anhydrous iron silicate, $SiO_4, Fe_2 = 2FeO, SiO_2$, and occurs in masses composed of dark green crystalline grains, exhibiting a reddish, or occasionally black, tinge. These crystals belong to the orthorhombic type; their hardness is 6·5, and the sp. gr. 4.

Fayalite gelatinises in presence of acids, and melts before the blowpipe to form a black magnetic bead. It is formed artificially during the smelting of iron ores in blast furnaces, and also during the refining of crude copper.

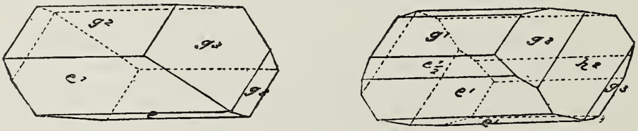
B. CHLOROPHŒITE is a hydrated ferrous silicate containing a little magnesia, and forming small, fibrous or compact, translucent or opaque, pistachio-green or black masses, and is also found as crystalline needles. It has been met with in a green amygdaloid rock among the basalts of the Isle of Rum, and in Fife. The hardness varies between 1·5 and 2, and the sp. gr. from 1·8 to 2.

C. KNEBELITE.—A ferro-manganous silicate ($MnFeSiO_4$), forming crystalline or amorphous masses, grey, reddish, brown, or green in colour, in Ilmenau granite and the iron deposits of Danemora (Sweden). Hardness, 6·5; sp. gr., 3·7 to 4·1.

D. HISINGERITE is an iron hydrosilicate of variable composition, containing ferrous and ferric oxides, and forming compact masses (hardness, 3; sp. gr., 3·04) at Riddarhyttan (Sweden), Bodenmais (Bavaria), etc.

E. NONTRONITE.—A hydrated ferric silicate forming a straw-yellow, canary-yellow, greenish, or sometimes rose-red mineral, unctuous, tender enough to be scratched by the finger-nail, and readily soluble in HCl. It is found in renal masses at Saint-Pardoux in the Dordogne district, Andreasberg in the Hartz Mountains, etc.

81. **Multiple Silicates of Iron.**—*A.* ANHYDROUS SILICATES. —I. *Peridot.*—This is an orthosilicate of magnesium (Mg_2SiO_4), wherein a portion of the magnesium is replaced by iron in the state of ferrous oxide. The colour is a more or less brownish bottle-green; the fracture, conchoid and lustrous. It is transparent or translucent. The crystals have received the name of *chrysolite*, whilst the granular variety is known as *olivine*.

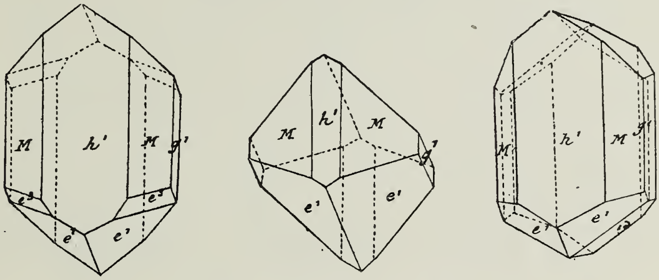


FIGS. 75 and 76.—Peridot.

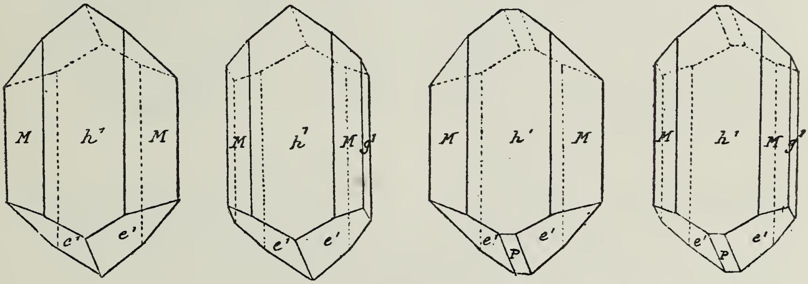
Peridot is infusible before the blowpipe, unless the proportion of iron is high; it is soluble in acids.

Hardness, 6 to 7; sp. gr., 3·1 to 3·5; crystalline form, the orthorhombic prism. The simplest crystals are those from Vesuvius and Puy, which exhibit none of the faces of the primitive form.

II. *Augite.*—Under this title are grouped the aluminous or other pyroxines of calcium and magnesium, in which the proportion of ferrous oxide exceeds 5 per cent., without, however, exceeding that of the magnesia.



FIGS. 77, 78, and 79.—Augite.



FIGS. 80, 81, 82, and 83.—Augite.

Augite, properly so called, is the pyroxine of lavas and basalts (Vesuvius, Auvergne). It is derived from an oblique rhomboid prism. The secondary forms of these crystals are prisms with six of the faces flattened in consequence of the enlargement of the modification h^1. The ends are generally formed of the sloping faces $e'e'$, which are well developed, any other facets forming part therewith being very small and without influence on the general contour of the extremity. The crystals are often macleated parallel to h^1.

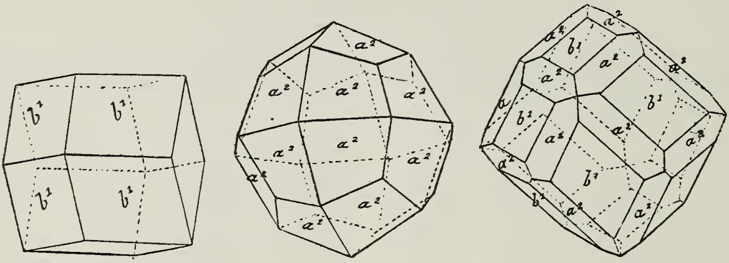
Augite is deep black in colour, with a sp. gr. = 3·3 to 3·4; hardness, 6.

III. *Hedenbergite.*—This is another variety of pyroxine, characterised by the substitution of iron oxide for magnesia. The formula is $(\mathrm{Ca}, \mathrm{Fe})\ \mathrm{SiO_3}$, but traces of magnesia are rarely absent. The hardness is 5·5, and the sp. gr. 3·5.

It is found in laminated masses with chalk, cupreous pyrites, quartz, and mica, near Tunaberg (Sweden).

IV. *Hypersthene.*—This mineral, which has often been classed with pyroxine, resembles the latter in composition and its angles of cleavage. The fracture is lamellar; the colour black or bronze-red. It is hard enough to scratch glass, and has a sp. gr. = 3·4.

V. *Almandin Garnet.*—This substance belongs to the garnet group, and is still known as the *Syrian* or *Oriental garnet* or *carbuncle.* The formula is $\mathrm{Fe_3Al_2Si_3O_{12}}$. It is the most abundant of the group, is of a fine red colour, and is employed in jewellery. Acids attack it with difficulty, and before the blowpipe it fuses to a black translucent, magnetic glass. The sp. gr. varies between 3·7 and 4·3, and the degree of hardness from 7 to 7·5.



FIGS. 84, 85, and 86.—Almandin garnet.

It crystallises in the cubic system, the most frequent forms being the rhomboid dodecahedron and the trapezohedron; crystals bearing the facets of both forms are also met with, whilst other forms, principally exhibiting the faces of the cube, are more rare.

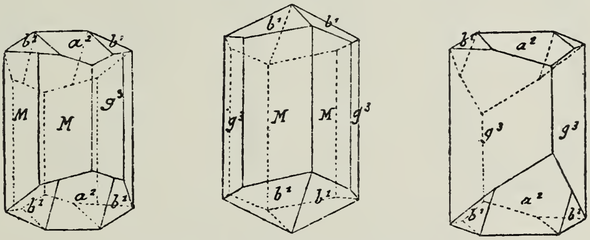
VI. *Epidote.*—The epidotes constitute an important family, whose members are differentiated by the proportion of the bases entering into their composition. They consist of an orthosilicate of alumina and lime, wherein part of the alumina is replaced by ferric oxide and part of the lime by ferrous oxide and magnesia.

The ferruginous epidotes seem to approximate to the mean formula

$$18CaO\ (4Fe_2O_3,\ 8Al_2O_3)\ 27SiO_2.$$

They crystallise in the clinorhombic system.

VII. *Ilvaite* (lievrite, yenite, calcareo-siliceous iron).—Ilvaite occurs as crystals, bacillary masses, or amorphous masses of a deep black colour. The fracture is resinous and somewhat bright.



FIGS. 87, 88, and 89.—Ilvaite.

The sp. gr. is 3·8 to 4, and the degree of hardness between that of glass (which it scratches) and felspar (by which it is scratched). It is faintly magnetic, fuses readily to an opaque glass before the blowpipe, and is soluble in HCl. In composition it is a silicate of iron and lime, with a little manganese and water.

The following oxygen ratio was deduced by Rammelsberg from personal analytical results:—

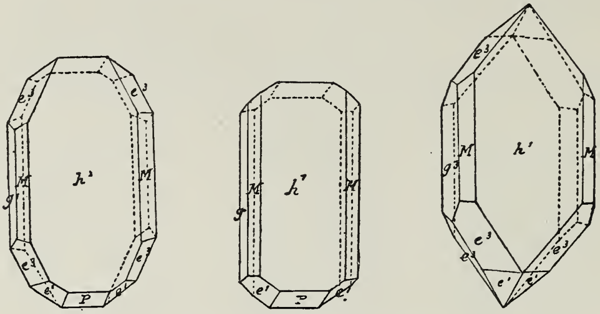
$$(RO + R_2O_3) : SiO_2 : H_2O = 9 : 8 : 0{\cdot}75.$$

The mineral is found in crystalline schists, with amphibole, quartz, etc., at Rio le Marina (Elba) and Kangerdluarsuk (Greenland).

The crystals of ilvaite are derived from the orthorhombic prism, and generally terminate in a wedge, the principal facet of which is a^2 (Figs. 87, 89). In nearly all the crystals the facets b make their appearance in proximity to a^2, and in some cases predominate, the crystals then terminating in quadrilateral pyramids (Fig. 88).

VIII. *Achmite* is a silicate of iron and sodium, containing a little Mn, titanic acid, and lime, and forming elongated, opaque, blackish-brown crystals, met with in Rundemyr granite (Norway), and exhibiting a vitreous lustre. It is slightly acted upon by acids, and fuses readily before the blowpipe to a black magnetic globule. The hardness is 6, and the sp. gr. 3·2 to 3·6.

The crystals of achmite are derived from an oblique rhomboid prism, the angles of which resemble those of pyroxine.



FIGS. 90, 91, and 92.—Achmite.

The prisms are octahedral, considerably flattened owing to the enlargement of the face h^1, and are mostly terminated by pointed extremities with four faces resulting from the modification e^3, with which is occasionally associated e^1 (Figs. 90 to 92). Basal crystals are also encountered, and frequently the crystals are macleated parallel to h^1.

IX. *Arfvedsonite.*—A ferro-sodium silicate remarkable for its high percentage content of iron. The crystals are imperfect, and probably isomorphous with those of amphibole.

X. *Wichtine.*—A silicate of alumina and ferrous oxide, forming black masses with an imperfectly conchoidal fracture, and found in the district of Wichtis (Finland).

B. HYDRATED SILICATES.—I. *Stilpnomelane.*—This is a hydrated silicate of iron with 5 per cent. of alumina, a little magnesia, lime and potash, found at Obergrund near Zuckmantel, in Silesia. It is attacked with difficulty by acids; gives off water when heated in a tube; has a sp. gr. = 3 to 3·4, and a degree of hardness = 3 to 4.

II. *Cronstedtite.*—A hydrated silicate of iron, magnesia, and manganese, occurring as reniform masses of divergent bacillar needles, of a handsome black colour, vitreous lustre, and opaque. Found at Przibram (Bohemia), and formerly looked upon as a variety of tourmaline.

This body is readily acted upon by HNO_3, nitrous fumes being evolved. The solution finally gelatinises. The degree of hardness is 2·5 ; the sp. gr., 2·35 ; and the powdered substance is dark green in colour.

The crystals are regular hexagonal prisms, or radial crystals forming orbicular kidneys, the constituent needles being triangular pyramids belonging to the tips of a sharp-pointed rhombohedron.

III. *Glauconite* (chlorite) consists of a ferrous hydrosilicate containing potash, lime, etc., but is of exceedingly variable composition.

PART II

MANUFACTURE OF ALUMINIUM SULPHATE AND SULPHATES OF IRON

CHAPTER III

Manufacture of Aluminium Sulphate and the Alums

§ 1. MANUFACTURE OF ALUMINIUM SULPHATE

82. **General Remarks.**—At a not very remote date aluminium sulphate was still regarded as merely a laboratory product, and it was only about the year 1845—when Pommier of Paris commenced to prepare it on a proper manufacturing scale—that this substance began to be used industrially. Difficulties were encountered at the outset, consumers hesitating to give up the alum to which they were accustomed, and which they could rely on obtaining pure, in favour of the amorphous, pasty, deliquescent, acid, and often impure product forming the aluminium sulphate manufactured at that date. This distrust was, moreover, heightened in consequence of certain mishaps (due to excessive acidity) that attended the employment of the new product as a mordant and in the sizing of paper; but as soon as a method of producing it in a neutral condition and free from iron was devised, aluminium sulphate was promptly adopted and substituted for alum in numerous branches of industry.

The reason is not far to seek. The various applications of alum are based on its content of alumina, which is barely 10 to 10·6 per cent., whereas aluminium sulphate contains from 14 to 16 per cent. Given equality of price, it is therefore more economical to employ the latter, which, besides being more soluble, is more convenient in use.

The raw material at first employed in the manufacture of aluminium sulphate was kaolin, together with other aluminous clays, but these have now been almost entirely abandoned. The utilisation of clays for this purpose is due to Curandeau, who founded works at Javel near Paris, about 100 years ago, and to Chaptal, who introduced it almost contemporaneously at Montpellier, though the object of these savants was not to prepare aluminium sulphate for direct use, but to convert it into alum by *brévetage* (Girardin, *Chimie elementaire*, p. 411).

Large quantities of impure aluminium sulphate are obtainable by treating pyritic shales and lignites, but—except perhaps in Belgium—this method of manufacture has now almost entirely disappeared. Other aluminous substances, notably aluminium phosphate, have also served in the preparation of this product, but at present scarcely any other raw materials are used but *alunite* and *bauxite*, from which some 12,000 to 14,000 tons of aluminium sulphate are now annually produced in France.

The French industry is not a very profitable one, owing to foreign competition, chiefly by the Germans, who, possessing better appointed factories and cheaper sulphuric acid and labour, are able to supply a purer article at lower rates.

Although the production of aluminium sulphate from kaolin and other clays is now a matter of little more than historical interest, it cannot be passed over altogether, and a brief description of these older processes will be given in the following pages, followed by a more detailed exposition of the treatment actually applied to alunite and bauxite for the same purpose.

83. **Production of Aluminium Sulphate from Kaolin, or Clay, and Sulphuric Acid.**—The principal deposits of kaolin are met with in Cornwall, and (in France) at St. Yrieix near Limoges, in the departments of Allier, Puy-de-Dôme, Brittany, etc. The composition of the different kaolins having been already given (Chap. I. § 3), need not be gone into again now.

According to Pommier (*Encyclopédie chimique*, vol. v.), "in preparing aluminium sulphate, a commencement is made by reducing kaolin to the finest possible state of division by milling and sifting, after which it is calcined for 2 to 3 hours in vaulted reverberatory furnaces, each holding from 4 to 6 cwts. (200 to 300 kilos.) of material. The object of this calcination is to peroxidise the iron present in the kaolin, and thus reduce its susceptibility to the action of acid; whilst, on the other hand, the alumina is rendered more open to attack if the calcination is not carried on at a too elevated temperature. Dull red heat is the most suitable. The calcined kaolin is taken out of the furnace by the aid of an iron vessel and turned, just as it is, into a cylindrical leaden pan holding 1200 to 1500 litres (265 to 330 galls.) and heated by a perforated steam coil. The charge consists of 200 kilos. (440 lbs.) of kaolin and 300 kilos. (660 lbs.) of 53° Bé. sulphuric acid, the latter being run in on the hot kaolin.

"The reaction commences immediately, and, to prevent the mass becoming too thick, water is added, the steam tap being at the same time turned on more fully. Care is taken to keep the mixture well stirred with a wooden paddle throughout the duration of the reaction, in order to ensure that no portion of the kaolin escapes attack. When the reaction is at an end the mass is left for 2 or 3 days to enable the liberated and precipitated silica to subside. The clear liquid, which constitutes a 20° to 25° Bé. solution of aluminium sulphate, is then syphoned off into a hemispherical leaden vessel heated by a steam coil, also of lead. In this vessel it is concentrated to a convenient degree, depending on the quality desired, and is then poured out into a crystallising pan or table of lead with turned-up edges.

"In cooling down the mass thickens rapidly, and is then divided into cakes of different sizes, by means of a wide-toothed, wooden rake, and left until quite cold, whereupon the cakes are separated and packed. This completes the process.

"To ensure that all the alumina contained in the kaolin is properly acted upon it is necessary to employ a larger quantity of acid than is theoretically requisite, the result of which is the presence in the finished product of a little free acid, which, however, is no drawback for certain purposes. Nevertheless, when a neutral sulphate is desired, the excess of acid can be neutralised during the stage of concentration by adding pure aluminium hydroxide prepared from cryolite. It is, however, important that an excess of alumina should be avoided, otherwise a basic sulphate will be formed, which, being naturally of a yellow colour, will tinge the entire mass and reduce its commercial value."

The various kinds of clay would be treated in the same manner. The process now possesses scarcely more than a historical interest, and need not be further dilated upon. It seems, however, that the *Société-Industrielle de Landenau* (Finistère) still manufactures aluminium sulphate from kaolin. The author is unaware of the details of the process employed by this firm, but it is probably similar to that pursued with alunite or bauxite, namely, the progressive exhaustion of the mineral by successive attacks in the manner described later on.

84. **Alum Cake.**—This product is merely a crude aluminium sulphate charged with silica, which is utilised in the manufacture of common qualities of paper. It is chiefly manufactured in England by treating kaolin or other clays. A variety of alum cake has also been prepared from bauxite.

The kaolin or clay, previously ground, is introduced in a hot condition from the calcining oven into a cast-iron pan. Hot 53° Bé. sulphuric acid is poured over the mass in the proportion of 150 parts (by weight) per cent., the reaction, which proceeds vigorously, being soon completed. The mixture is kept continuously stirred with iron stirrers, and the paste is cast in moulds or is divided into cakes before it has set hard. Thus prepared, the product contains the whole of the silica present in the raw material, which silica becomes incorporated with the pulp in paper-making and increases the weight.

85. **Manufacture of Aluminium Sulphate from Shale, Clay, and Sulphurous Acid.**—Sulphurous acid reacts with some energy on argillaceous substances, and produces aluminium sulphate therefrom. This reaction is evidently based on the conversion of the sulphurous acid into sulphuric acid when brought into contact with atmospheric oxygen. Ferric oxide, when present, also con-

siderably facilitates this transformation in virtue of its oxidising action.

The production of aluminium sulphate by means of sulphurous acid has long been carried on in certain localities, metallurgists who treat blende or galena having at hand a ready use for the sulphurous acid liberated during the roasting of these ores.

As an example may be cited the Ampsine works in Belgium, where De Laminne causes sulphurous acid to circulate through a series of channels practised in the interior of heaps of spent clay shales from the manufacture of alum. These spent shales contain—

Silica	63 per cent.	Magnesia	6 per cent.
Alumina	18 ,,	Potash, etc.	
Iron oxide	13 ,,		

They are obtained by treating *ampelite*, an aluminiferous rock first discovered at Amay, and subsequently detected over an area of 2 to 3 miles in length between Flemalle and Autheit, *viâ* Flône and Ampsine. Here the rock forms the oldest bed of the coal measures, and is 20 to 45 feet in thickness, dipping towards the south at an angle of 70°.

The average composition is—

Silica	60·0 per cent.	Pyrites	7·0 per cent.
Alumina	17·0 ,,	Lime and Magnesia	5·0 ,,
Potash	2·5 ,,	Carbonate of iron	4·0 ,,
Carbon	4·5 ,,		

This mineral was treated in numerous factories, 18 of which were in full activity in 1808, and dealt, on a average, with 12,000 cubic metres (15,700 cubic yards) per annum. The rock was roasted in the open air, then carefully lixiviated, and the residue discarded. In the process followed by De Laminne, these residues, when brought into contact with sulphurous acid, absorb it entirely. When the mass is sufficiently converted into aluminium sulphate it is lixiviated, the liquor being then concentrated and cast in cakes in the usual manner. The product is impure, containing an excess of sulphuric acid and ferric sulphate (about 3 to 6 per cent.), and in this condition is restricted to a very limited sphere of utility.

De Laminne has, however, succeeded in purifying it by heating spent shale on the bed of a reverberatory furnace, and incorporating it with the solution of crude sulphate so as to obtain a thick pulp. The reaction set up is expressed by the equation

$$(SO_4)_3Al_2 + Al_2(HO)_6 + (SO_4)_3Fe_2 = 2[(SO_4)_3Al_2] + Fe_2(HO)_6.$$

After a certain period of repose the mass is extracted with water and the solution concentrated.

86. Production of Aluminium Sulphate from Argillaceous and Pyritic Lignites.—This process, which had its day, is now almost entirely obsolete, there being only one factory in France—and that of small importance—where it is still in use.

The object of this industry was not so much to provide a commercial aluminium as to furnish alum makers with a product suitable as a raw material for their purposes. This very impure article was known as *magmas*.

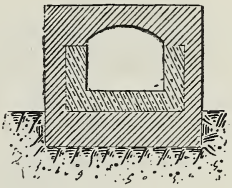


FIG. 93.

The argillaceous lignites, a more detailed account of which will be given later, were mixed and piled up in prismatic heaps on a level open space, whereupon the contained pyrites began to oxidise. The heaps were then ignited and left to burn, the oxidation of the pyrites proceeding vigorously under the influence of atmospheric oxygen, and furnishing sulphurous acid which attacked the clay. The iron sulphate formed was itself decomposed by the high temperature prevailing, and yielded sulphurous acid and sulphur trioxide, which combined with the clay and left a residue of ferric oxide. Finally, a red mass known as *red ash* was obtained, comparatively rich in aluminium sulphate, and containing but a small quantity of iron (ferric) sulphate.

This mass was lixiviated in wooden or dressed stone vats provided with false bottoms, covered with brushwood to serve as a filtering medium.

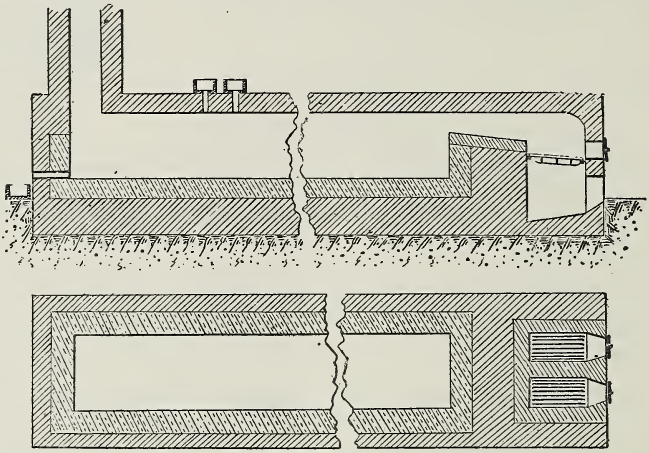
The filtered liquor was concentrated to 42° to 44° Bé. in large brickwork chambers, and then poured into crystallising pans, where it solidified to a pasty mass rich in aluminium sulphate.

The concentrating chambers were about 50 to 65 feet long, and 40 to 60 inches wide, and the depth of the liquor varied between 20 to 30 inches. The hearth was separated from the chamber by a sloping bridge about 60 inches long, intended to prevent the conveyance of ash into the chamber and to keep the liquor from direct contact with the flame (see Figs. 93 to 95).

The aluminium sulphate obtained by this process exhibited the following average composition :—

Anhydrous aluminium sulphate	36·00	Calcium sulphate	0·20
Ferric sulphate	5·00	Water and undetermined matters	58·40
Ferrous ,, ...	0·40		

Frequently it contained a notable quantity of alum, due to the presence of a certain quantity of potash in the lignite, and the absorption, during evaporation, of the ammonia present in the furnace gases.



FIGS. 94 and 95.—Reverberatory evaporator for liquor to be converted into *magmas.*

87. Manufacture of Aluminium Sulphate from Pure Alumina, derived from Cryolite or Bauxite.—Cryolite is a double fluoride of aluminium and sodium. It may be employed for the production of soda, with which object it is treated with quicklime or calcium carbonate, either by the wet or dry process, the result of which is the formation of sodium aluminate and calcium fluoride. The mass is then extracted with water, which dissolves out the aluminate and leaves the fluoride behind. On treating the solution with a current of carbon dioxide, pure alumina is precipitated, whilst sodium carbonate is left in solution. This alumina, which forms a waste product, can be advantageously utilised for the production of aluminium sulphate, an industry that is principally centred in Northern Germany. The alumina obtained from the treatment of cryolite is almost chemically pure, being entirely free from silica, iron, and all impurities, except a certain—and by no means unimportant—quantity of sodium carbonate.

To prepare aluminium sulphate from this material a leaden pan is charged with 53° Bé. sulphuric acid, which is then heated by steam to a temperature of 80° to 90° C. The alumina is added gradually until the acid is saturated, by which means a concentrated solution of pure aluminium sulphate—containing a little sodium sulphate—is obtained; this liquor is drawn off and cast into moulds after concentration. The resulting aluminium sulphate is very fine, and gives no blue coloration with potassium ferrocyanide.

An analogous product has been prepared from bauxite, the pure alumina being obtained from the intermediate stage of sodium aluminate. A large quantity of aluminium sulphate is manufactured in France by this method at the Salyndres works.

The bauxite, reduced to a fine powder, is mixed with sodium carbonate and placed in a reverberatory furnace, where it is strongly heated and well stirred until the whole of the sodium carbonate has been attacked, the operation taking about 5 hours. The aluminate is then lixiviated by successive extractions, first with weak liquor from a previous batch, and finally with pure water. The liquors are kept separate, the stronger solution being stored, whilst the weaker final runnings are used over again.

The operation is performed in a cylindrical vessel of sheet-iron with a perforated false bottom of the same metal covered by a cloth (see Fig. 96), the top of the filtering vessel being closed by a tight-fitting metal cover. To work the apparatus, a charge of about $\frac{1}{2}$ ton of aluminate is placed on the filter, the cover is fastened down, and steam under pressure is blown into a closed tank (F, Fig. 96), containing the weak liquor from a previous operation and communicating with the upper division of the filtering vessel by a pipe dipping nearly to the bottom of the tank, thus forcing the weak liquor up into the former vessel. Steam is injected to heat the contents of the filter quickly, and the strong solution collecting below the false bottom is drawn off through a tap. When the density of the extract falls below 4° Bé. the liquor is set aside as "weak," and pure water is introduced through a separate feed pipe. The average strength of the strong liquors is about 12° Bé.

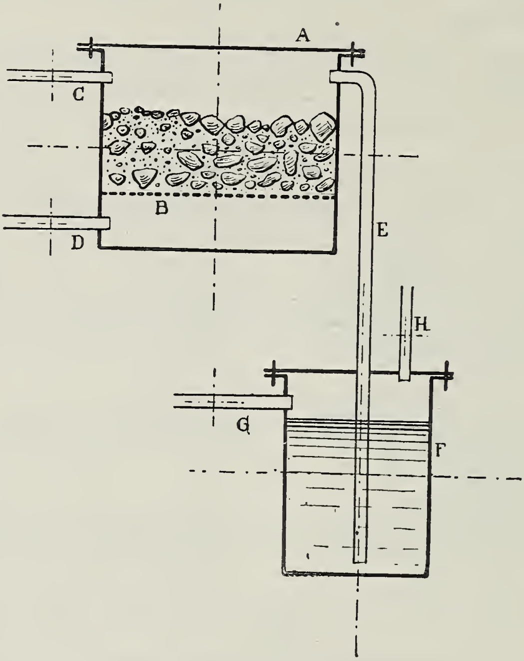


FIG. 96.—Lixiviation of crude aluminate.

A, Filtering vessel; B, filtering surface; G, steam inlet pipe; F, weak liquor tank; E, pipe delivering weak liquor to filtering vessel; C, steam pipe for heating filter; D, outlet pipe; H, feed-water pipe.

These liquors are run into a boiler (Fig. 97) forming part of the precipitation plant, where they are treated with a strong current of carbon dioxide produced either by the combustion of coke, decomposition of chalk by heat, or by the action of HCl on the last-named substance. Each boiler holds about 1200 litres (265 galls.) of solution, and is fitted with an agitator for keeping the contents continually in motion. Whilst the operation is in progress steam is admitted, to raise the temperature of the liquid to 70° C. The introduction of the CO_2 is arranged so that the current enters the vessel containing the most exhausted liquor first, methodical precipitation being thereby ensured.

The resulting precipitated alumina and the dissolved sodium carbonate are collected in a reservoir underneath each vessel. The solution is then decanted, and concentrated for the recovery of the salt employed, *minus* waste, whilst the alumina is drained in a hydro-extractor; and, after being clarified by the aid of pure water, is treated with sulphuric acid in the manner already described, pure aluminium sulphate being obtained. The method is, however, an expensive one.

Cheaper processes have been devised for obtaining alumina from aluminates, and among them the interesting method originated by Baeyer should not be overlooked. This method is based on the discovery that when a solution of sodium aluminate is agitated with a small quantity of freshly precipitated aluminium hydroxide—such as is formed by the action of carbon dioxide on aluminate solution in the cold—the precipitate of alumina goes on increasing, and at the end of a certain time only a small proportion of alumina (1 molecule per 6 mols. of soda) is left in solution.

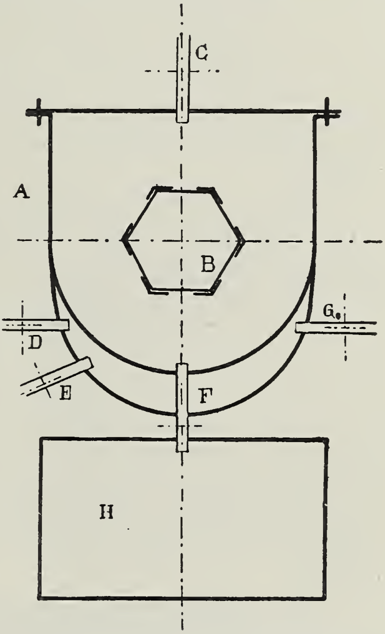


FIG. 97.—Carbonating the aluminate solution.

A, Pan; B, agitator; G, steam pipe; C, feed pipe for aluminate solution; E, blow-off; D, CO_2 pipe; F, effluent; H, reservoir.

This reaction may be observed when a solution of aluminate is agitated out of contact with carbon dioxide; and it must be borne in mind during the lixiviation of calcined bauxite with soda, since the residue may easily retain alumina precipitated in this manner.

The following are the result of sundry experiments made by the author:—

A clear solution containing 63·49 grms. of alumina and 66·96 grms. of soda (Na_2O) per litre was treated with a little aluminium hydroxide and shaken up cold in a corked flask; precipitation ensued, the liquid gradually becoming poorer in alumina in the following proportion:—

After 48 hours the solution contained 35·78 grms. of Al_2O_3 per litre,
,, 62 ,, ,, 29·44 ,,
,, 110 ,, ,, 21·80 ,,
,, 134 ,, ,, 15·50 ,,

but no decrease followed when the agitation was further prolonged.

With a solution (4000 litres) containing 61·95 grms. of Al_2O_3 and 70·68 grms. of Na_2O per litre the same treatment gave the following results:—

At the end of 12 hours, 49·42 grms. of Al_2O_3 per litre,
,, 24 ,, 39·78 ,,
,, 36 ,, 33·97 ,,
,, 48 ,, 29·00 ,,
,, 72 ,, 23·68 ,,
,, 84 ,, 17·80 ,,

This curious reaction, which occurs solely in the case of alumina precipitated from the aluminate, is difficult of explanation.

The industrial application of the process is a matter of great interest: on the one hand, it dispenses with the employment of carbon dioxide, and, on the other, the alumina is free from silica and phosphoric acid, neither of which is thrown down; furthermore, the reaction occurs in the cold and requires no apparatus beyond an agitator; and, finally, the liquids used furnish much better results in the treatment of bauxite than are obtainable from the sodium carbonate usually employed.

Moreover, it is convenient to dispense with this carbonate and to repair the waste of alkali by an addition of caustic soda. By this means it becomes possible to work with quantities absolutely in accordance with theoretical calculations, and the yield of alumina is considerably increased (*Dict. de Wurtz*, 2 Suppl. p. 185).

The Baeyer process is in use at the Larne Harbour Aluminium Factory, where it is employed in the preparation of pure alumina for conversion into aluminium.

The raw material is Antrim bauxite, containing—

Alumina	56 per cent.	Titanic acid . . .	3 per cent.
Ferric oxide . . .	3 ,,	Water	26 ,,
Silica	12 ,,		

The ground mineral is calcined in a roasting furnace of the Oxland and Hocking type, and consisting of an iron pipe 33 feet long by 3¼ feet in diameter, coated with firebrick and mounted on trunnions so as to be capable of receiving a rotary motion. The pipe is mounted on the slope, and heated by a fire placed at the lower end, the hot gases traversing the pipe and escaping into a smokestack at the farther end. The mineral is fed continuously in at the top, and, by the assistance of the rotary movement of the furnace, is discharged in a roasted condition at the other end, on to a platform provided with an aperture just large enough to allow the passage of the lumps. Thence it falls into a second pipe 30 feet long by 2 feet 6 inches wide, placed beneath and sloping in the opposite direction, where it is cooled down in a current of air blown in by a fan. The roasted mineral is next ground fine enough to pass through a sieve with 30 meshes to the linear inch.

Thus prepared, the bauxite is exposed to the action of caustic soda solution in tanks provided with holes for introducing and removing the charge, and also with safety valves and inlet and outlet pipes for steam and water respectively.

The soda solution has the sp. gr. 1·45, and is put into the tanks before the bauxite, which is then added slowly, the mass being kept stirred. Steam is next turned on, and a pressure of 70 to 80 lbs. per square inch is maintained for 2 to 3 hours, after which the tanks are emptied into reservoirs at a higher level, where the solution is diluted to 1·23. A passage through the filter-press separates a red residue, for which no application has as yet been found. The washings of this residue are united with the main solution, which is then clarified by passing it through wood shavings.

The precipitation of the alumina is effected, as already described in the Baeyer process, by agitating the solution in presence of a certain quantity of freshly prepared alumina. For this purpose the requisite quantity of aluminium hydroxide is introduced into a circular decomposing tank, the aluminate solution being then run in and the whole kept in constant agitation. At the end of 36 hours, 70 per cent. of the alumina will have come down, whereupon the agitation is suspended, the weak liquor drawn off and stored, and the alumina is passed through the filter press, washed and dried.

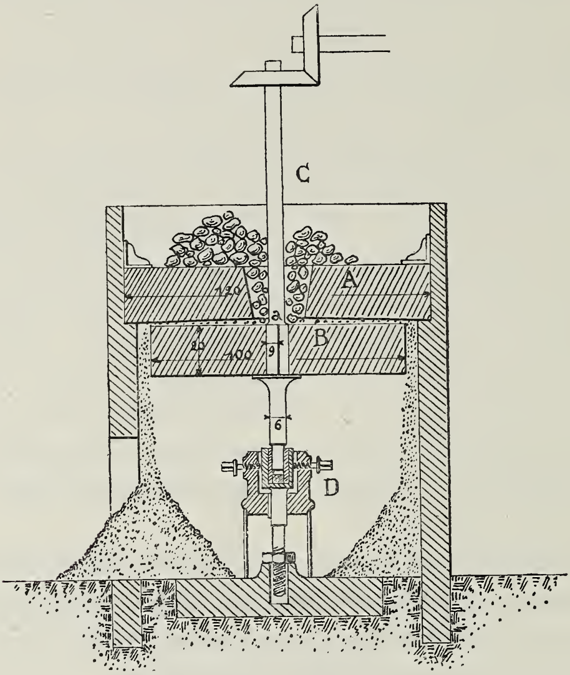


FIG. 98.—Grinding mill.

The residual liquor, which has a density of 1·2, is concentrated in triple-action concentrators to 1·45, and is then used over again for attacking the mineral (*Moniteur Scientifique*, 1897, p. 596).

88. **Treatment of Bauxite.**—*A*. GENERAL REMARKS.—Bauxite and alunite form the most important minerals at present employed for the production of aluminium sulphate. The methods briefly described above are now no longer employed,

except perhaps the one wherein the alumina is precipitated from aluminates and furnishes a product entirely free from iron, and the one in which shale is attacked by sulphurous acid.

Although simple, the treatment of bauxite is a somewhat delicate operation, and never furnishes products of the same degree of purity as those yielded by alunite.

In connection with this subject the author is indebted to M. Lacarrière, chemical manufacturer, Noyon, for a mass of information on the treatment of bauxite, and for opportunities of examining the method pursued in his works.

The mineral used in France comes from the south, and costs 18 to 20 francs (14s. 6d. to 16s.) per ton on trucks at the mines. The composition of the aluminium minerals having been already described, all that need now be said is that the sellers guarantee a minimum content of 60 per cent. of Al_2O_3, and a maximum percentage of 3 per cent. of Fe_2O_3, the average composition supplied, to keep within these limits, being—

Alumina .	62·5 to 65·00 per cent.
Ferric oxide . . .	2·90 ,,
Calcium carbonate .	5·10 ,,
Matters insoluble in H_2SO_4,	10·50 per cent.
Loss at red heat . . .	19·00 ,,

The bauxite is delivered in lumps about the size of the fist, and has to be broken down and then ground.

B. Preparation of the Mineral. — The material is pulverised by a series of very hard millstones (Fig. 98). The upper stone A is rigidly mounted in a wooden frame fixed in strong masonry, and is pierced in the centre by a cylindro-conical aperture, the smaller diameter of which measures 8 inches, to allow of the passage of the driving shaft C, and of the material to be treated.

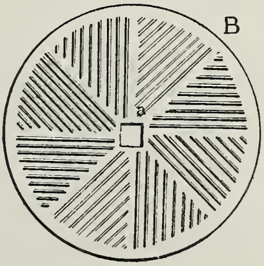


Fig. 99.—Face of the millstones.

The movable millstone B is carried by the shaft C, on which it is rigidly mounted at *a*, and which runs on a socket bearing D. The distance between the two stones is adjusted by the special arrangement figured in the sketch. The stones are dressed with grooves, as shown in Fig. 99.

The material to be ground is thrown on to the stationary millstone and falls through the feed aperture E, whence it makes its way between the stones and is discharged at the periphery in the state of more or less finely divided grit, which in turn has to be subjected to the operation of grinding, properly so-called.

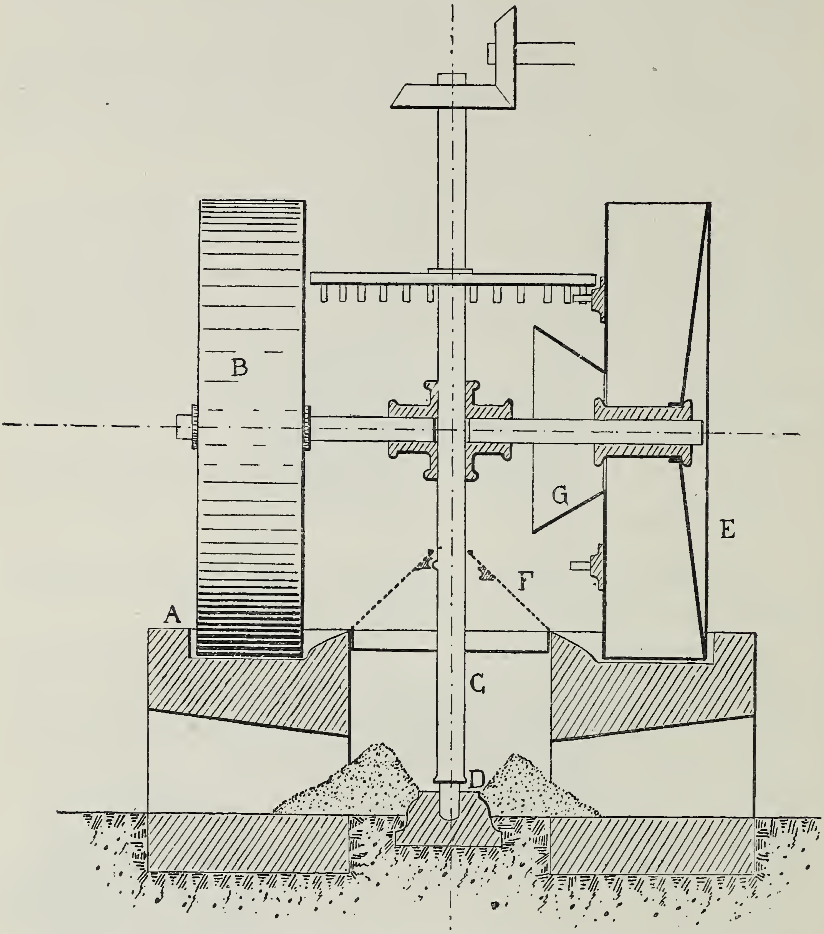


FIG. 100.—Mill for grinding and sifting bauxite.

The apparatus is comparatively economical, a mill of the following dimensions—

Diameter of upper stone	48 inches.
,, lower ,,	40 ,,
,, shaft	$2\frac{1}{8}$,,
,, square shank A	$3\frac{1}{2}$,,
Thickness of stones	8 ,,

being able to crush 15 to 20 tons of mineral per 12 hours shift, at an expenditure of 3 to 4 h.p. In the case of bauxite, the chief inconvenience arises from the rapid wear of the stones on account of the hardness of this material.

As a rule, however, the bauxite is not subjected to any preliminary crushing, but is ground at one operation in special mills. At the Noyon works the ingenious though uneconomical apparatus shown in Fig. 100 is used.

This consists of a small circular bed-plate A, of cast-iron or hard stone, on which rotates a cast-iron or hard stone runner B, which may also consist of a brickwork centre with an outer ring or tyre of metal. The runner is set in motion by a central shaft C revolving in a socket bearing D.

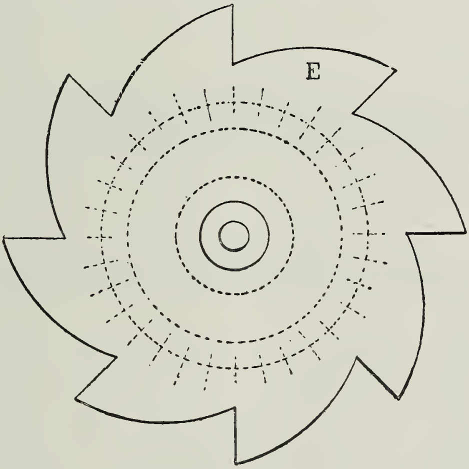


FIG. 101.—Collector.

Behind the runner is a collector E (shown separately in Fig. 101), which is turned by a train of cogwheels and collects the crushed mineral, which it then delivers through a hopper G on to a truncated conical screen F, shaken automatically by a cam on the shaft C. The unsifted portions are returned to the bed-plate by a scraper attached to the shaft C; whilst the fine powder is discharged into a hollow below the mill. The entire apparatus is enclosed in a sheet-iron case, to prevent inconvenience to the workmen from the dust. This mill will grind about 4 cwt. per hour, fine enough to pass through a No. 60

sieve, at a cost of about 5s. to 6s. 6d. per ton, which is rather expensive.

It is necessary to reduce the material to a very fine powder, otherwise the subsequent chemical reaction goes on very slowly and imperfectly. The ground powder is ready for immediate treatment, roasting being unnecessary, because bauxite is in itself a readily attackable aluminium hydroxide, and the little iron present is already in the state of ferric oxide and sparingly soluble in acid.

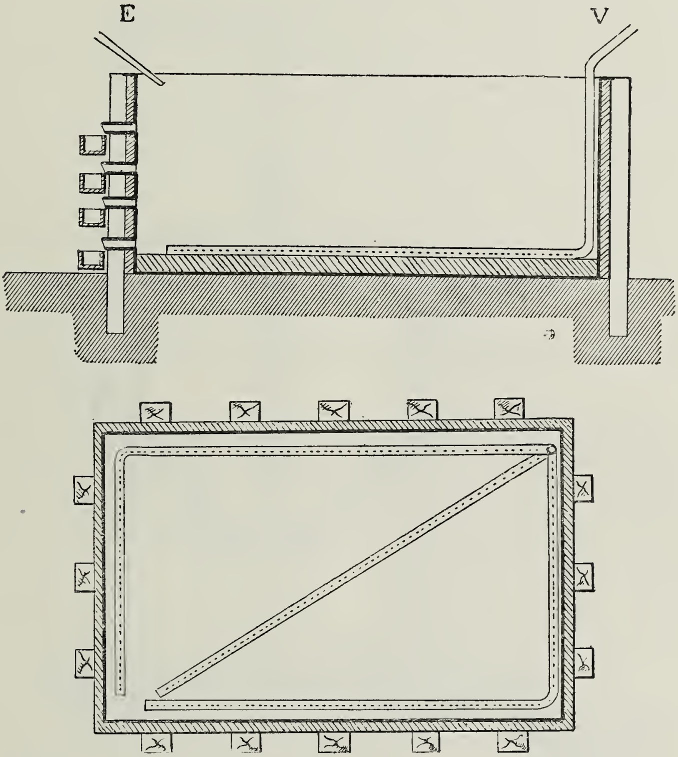
C. CHEMICAL TREATMENT.—The process, though simple, requires attention and constant supervision to ensure economy of manufacture, the loss of alumina in the residues, the degree of neutrality of the finished sulphate, and the consumption of fuel all depending on the care with which the chemical treatment is carried on.

The operation is effected in wooden vats lined with sheet-lead about ¼ inch thick, and heated internally by injecting steam through perforated leaden pipes (V, Fig. 102) running along the bottom of the vat, which is covered with planking to protect the lead lining from the perforating effect of the high-pressure jets of steam.

Three outlets, closed by plugs, are situated at different levels in the side of the vat, for drawing off the liquor, etc., the first being about 27 inches from the bottom, the second about 12 inches lower, and the third on a level with the bottom itself (Figs. 102, 103).

The vats have the following dimensions: width, about 10·8 feet; length, about 13·7 feet; depth, 5¼ feet; cubical capacity, 780 to 810 cubic feet. The weight of the leaden lining is about 2½ tons, and the total cost £72 to £80 per vat. Of course these dimensions need not be rigidly adhered to, and are merely quoted to give an approximate idea of the installation. Two vats of the above size will be sufficient for a works producing 1200 tons of aluminium sulphate per annum.

With such an installation a staff of four workmen is required, three of whom are employed for stirring the boiling mass with wooden paddles. The chemical reaction progresses very favourably; nevertheless, as it partly depends on the way in which the stirrers perform their task, and as the stirring, however carefully they may work, is always defective, owing to the difficulty of keeping the mineral matter in suspension and preventing its accumulation in corners, it follows that the production of a neutral solution is difficult and the extraction is imperfect, thus causing a loss of acid and alumina. Attempts have therefore been made to design more suitable apparatus, one of which, in use at the Noyon chemical works, is shown in Fig. 104.



FIGS. 102 and 103.—Rectangular vat, in plan and longitudinal section.

The principal feature of this plant is a cylindro-conical tank of thin sheet-lead lagged with wood, the cylindrical part measuring 11½ feet across and 8½ feet high, whilst the truncated cone, which is 46 inches in smaller diameter and of equal depth, forms the bottom of the apparatus (see Fig. 104).

The base is lined with pumice—a matter of some importance, because the jet of steam is generally situated there, and the unprotected lead would very soon get worn through. There are four outlets for drawing off the contents of the vat; the top one being about 40 inches below the upper rim, the second 84 inches, the third 8 feet from the top, and the fourth at the very bottom.

Steam is admitted through a vertical lead pipe A, which is suspended by a pulley *a*, whilst a second pipe B, supported by another pulley *b*, is mounted beside the first one and extends nearly to the bottom of the vat. This second pipe is connected with a Koerting injector, and serves to blow air through the contents of the vat and maintain constant agitation so as to keep the mineral matter in suspension during the whole of the chemical process.

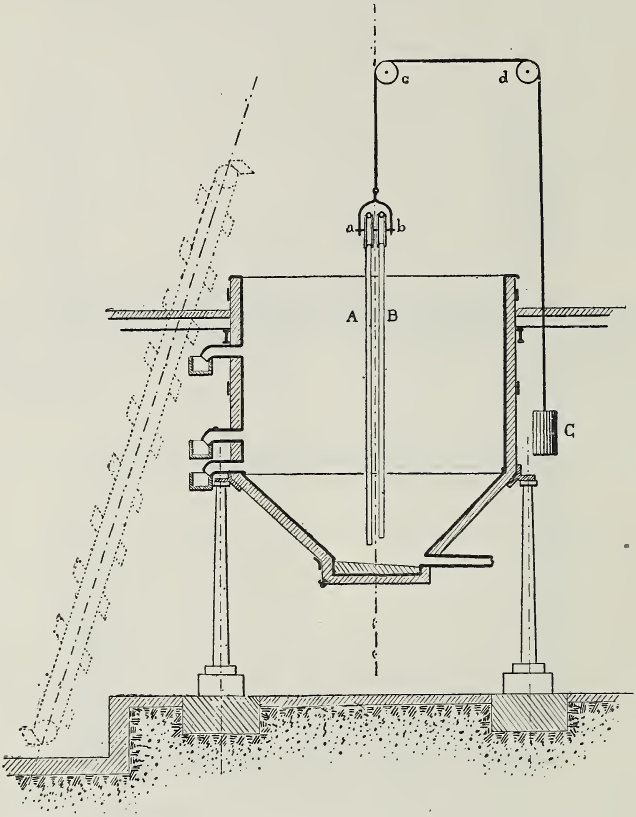


FIG. 104.—Cylindro-conical vat, with automatic air-blast agitator.

The pulleys *a* and *b* are mounted on a fork, which in turn is supported by a chain passing over two pulleys *c* and *d*, and terminating in a counterpoise C. The system is thus kept in equilibrium, and the vertical adjustment of the pipes in the vat becomes an easy task. A vat of the above description costs about £240.

The mineral is fed in by means of the elevator shown by dotted lines at the one side of the figure.

This system of installation has numerous advantages. The constant agitation by the air blast, and the cylindro-conical shape of the vessel, combine to prevent the accumulation of deposited mineral, and a more intimate contact between the ingredients is produced. The reaction goes on more rapidly, a condition of neutrality is more quickly reached; and, with a smaller quantity of sulphuric acid, the conversion of the materials is more complete and the residue more effectually extracted. Furthermore, a by no means inappreciable saving of labour is effected, since, in place of the four men needed for working the rectangular vats, one man will suffice.

Whichever system be employed, the progress of the reaction is the same.

Thus, for example, if we now take into consideration the rectangular vats,—leaving the cylindrical system until the alunite process is discussed,—a calculated quantity of an acid solution of aluminium sulphate from a previous treatment is put into one of the vats. The solution has a density of 35° to 40° Bé., and contains 250 to 300 grms. of SO_3 per litre. The charge measures about 350 cubic feet, which corresponds to 2½–3 tons of sulphuric acid, calculated as SO_3.

Heat is applied by injecting steam, and as soon as the liquor is hot the corresponding weight (*e.g.* 3 to 3½ tons) of the powdered mineral is added, the whole being mixed by the aid of wooden rakes, the heating and agitation continuing for 7 to 8 hours on end. The mass, which will then be (or should be) nearly or quite neutral, is next diluted and left at rest to clarify, the unattacked mineral depositing on the bottom of the vat. On the following day the liquor is decanted and transferred to leaden cisterns, wherein it deposits the final traces of matter in suspension before passing to the concentrators. This liquor has a density of about 32° Bé., and constitutes a neutral, or nearly neutral, slightly ferruginous solution of aluminium sulphate. The residue is lightly washed with fresh water, which is then run into the cisterns, the residue being afterwards treated with a highly acid liquor at 45° Bé. With this it is heated, stirred up, left to subside, and separated by decantation. The final attack is made with 60° Bé. sulphuric acid assisted by heat, and, towards the end, by an addition of acid liquor from a preceding batch.

After subsidence and decantation, the residue, now practically exhausted but still impregnated with liquor rich in sulphuric acid, is first washed in the extraction vat with weak (5° to 10° Bé.) liquor. This being decanted, the muddy residue is run off into cisterns and exhausted with water.

All the grades of liquor—except those from the first treatment, which are concentrated direct—are used over again, either for attacking the mineral or in washing.

The chief difficulty in this process is the decantation. In the case of bauxite the liquors do not clarify readily, and in general, to obtain satisfactory deposition, it is necessary not to employ too large a proportion of mineral. On the other hand, an excessive deviation in the contrary direction, so as to produce very weak liquors, leads to an excessive consumption of fuel for the evaporating pans. Thus it is evident that there is a medium course, which will have to be decided by practical experience in each particular case. The proportions already given are averages from satisfactory workings, but will necessarily vary according to the class of mineral treated. As far as possible the liquor should clarify sufficiently between night and morning, a condition not always realised when bauxite is used. Filter-presses have been resorted to for the purpose of accelerating the work, facilitating washing and diminishing the amount lost in the residues, but without success, the pores of the filtering medium being speedily clogged by the small quantity of clay and finely divided silica in the sediment. The amount of residue obtained varies according to the manner in which the work is performed, and generally fluctuates between 20 and 25 per cent. of the raw material taken. It consists mainly of silica, a little clay, about 8 to 10 per cent. of alumina, and a little ferric oxide. The quantity of alumina lost in the residue in normal working is therefore about 2 per cent. of the mineral employed—a fairly low proportion.

According to the quality of aluminium sulphate produced, and the more or less satisfactory performance of washing, the treatment of a ton of bauxite entails a consumption of 45 to 50 cwt. of 60° Bé. sulphuric acid, the yield being about 4 tons of aluminium sulphate.

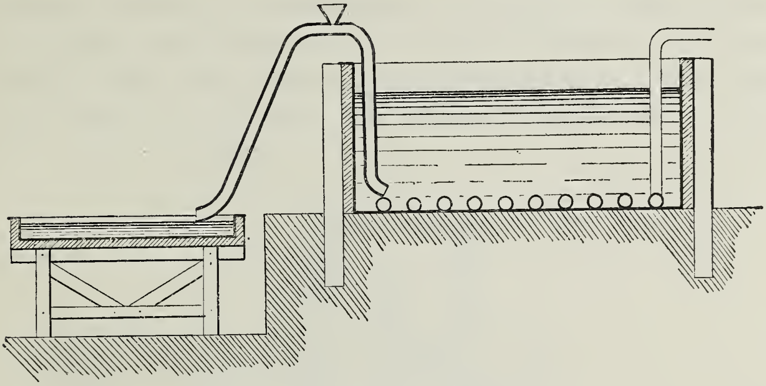


FIG. 105.—Concentrating the liquor.

D. CONCENTRATING THE LIQUOR.—The final stages of the work present no special difficulties. The liquid, which has a density of 33° to 34° Bé., from the treatment of the fresh mineral, is drawn off and evaporated in leaden vats heated by steam (Fig. 105).

FIG. 106.—Cutting rake.

Those employed at Noyon measure 12·8 feet × 4·25 feet × 40 inches, and are heated by a leaden coil $1\frac{1}{3}$ inches in diameter ($\frac{1}{5}$ inch metal), forming 10 rings of 32·8 feet each, thus giving a heating surface of about 118 square feet. These figures are, of course, not invariable; but, to ensure satisfactory working, the heating surface should be at least 2 square feet per cubic foot of vat capacity.

When sufficiently concentrated, the liquor is drawn off through a syphon on to leaden tables in front of the concentrating pans, the edges of the tables being turned up slightly all round to prevent the liquor from running over. Here it is left to cool; and as soon as a certain consistency has been attained the mass is divided, by means of a cutting rake with 3 or 4 teeth (Fig. 106), into cakes about 8 or 9 inches square, which are then stored. The extent to which the concentration of the liquor is carried depends on the quality of product in view. For common grades of low percentage the final strength of liquor is 46° Bé., whilst for the ordinary quality of cakes, lumps, etc., known as second whites, it is concentrated to 48°–50° Bé., and poured out to a depth of 4 to 5 inches on the crystallising trays. This product contains 12 to 13 per cent. of alumina. When concentrated to 52° Bé. the liquor furnishes a sulphate containing 14 per cent. of alumina. For the purest kinds to be subsequently powdered, the concentration is carried to 56°–58° Bé., and the depth of liquor on the crystallising trays is not more than about 2 inches: in this case the product contains about 16 per cent. of alumina.

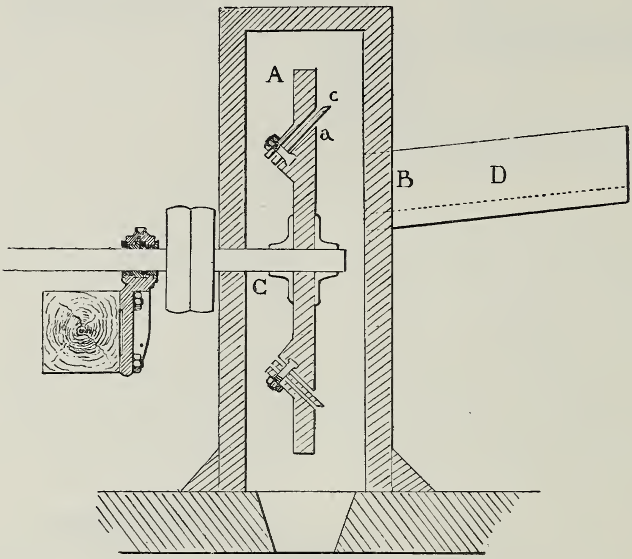


FIG. 107.—Pulveriser. Cross section.

E. TREATMENT OF THE FINISHED ALUMINIUM SULPHATE.—The ordinary kinds are usually reduced to coarse powder in a pulveriser (Figs. 107 and 108) consisting of a vertical disc A mounted on a shaft C, and provided with 6 oblique slits *a*, in which are bolted the rasp blades *c* (Fig. 109). This disc is set in a wooden case containing at one side an aperture B coinciding with the one end of a trough D, into which the blocks of sulphate to be pulverised are placed by hand and pushed in succession against the teeth of the disc, which runs at high speed. This apparatus works well, but takes a considerable amount of motive power.

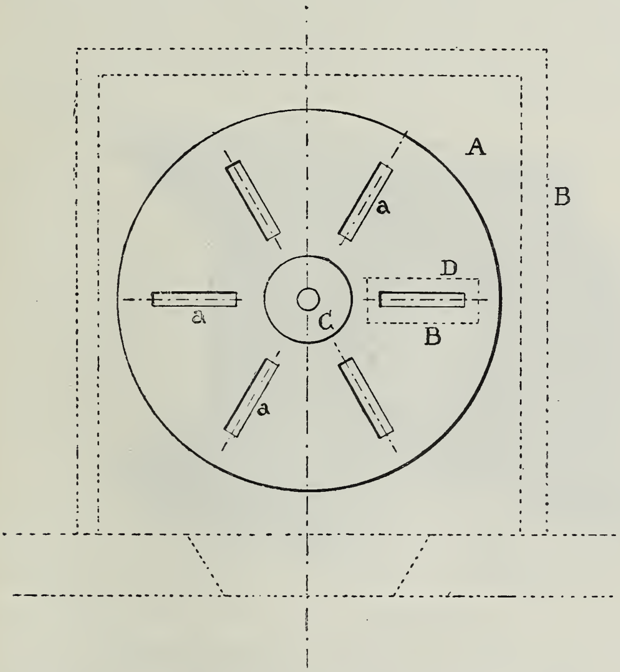


FIG. 108.—Pulveriser for aluminium sulphate. Front view.

FIG. 109.—Blade of pulveriser.

The grades destined to be converted into fine powder are put through a special mill. The trip-hammer mill, invented by L. Loiseau (maker, F. Weidknecht of Paris), has been seen at work by the author, and gives very good results; and the new pattern (Weidknecht and Schoeller system) now described is also highly satisfactory. These mills contain an arrangement of articulated hammers or beaters, oscillating upon axes and striking in their flight the material fed through the hopper (Fig. 110).

The object kept in view by the inventor is the imitation of hand labour; for, just as the stonebreaker employed on the roads is armed with a flexible-handled hammer, so this machine is provided with flexible hammers intended to produce the identical effect attainable by hand. These movable hammers, working at a certain speed, strike the material introduced through the hopper and break it into pieces of various sizes.

These pieces are projected, by the shock, against the massive head-piece of the machine, and, as they meet in their upward flight other fragments that are by this time descending, further breakage ensues without additional consumption of energy, this being the result of the projection. The materials then fall on to the hammers again and are caused to travel over steel grids which act as screens, the current of air set up by the motion of the hammers assisting the sifting action of the screens, which allow all the finer particles to pass away. The hammers then act as scrapers, removing all the insufficiently triturated material, and the process continues until the task is completed.

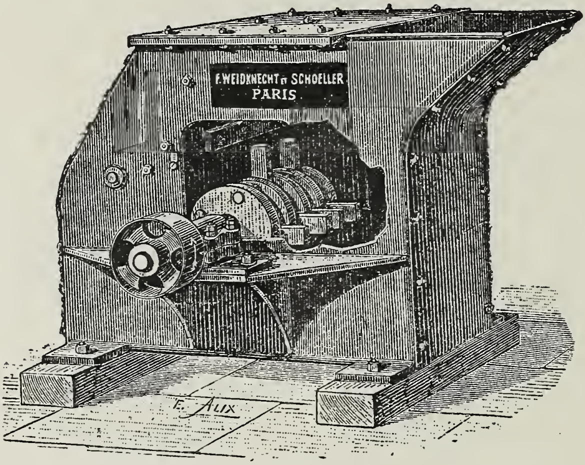


Fig. 110.

This operation also enables an intimate mixture to be obtained of products of different density.

Being loosely mounted, the hammers simply oscillate on their axes, and give way if the resistance to be overcome is excessive: thus all danger of breakage is prevented, the more so since there is no contact between the hammers and any other part of the machine. This method of action furnishes, among other advantages, that of ability to reduce certain products to an infinitesimally fine powder when required—or inversely—, a valuable consideration sometimes.

The hammers being loose, but little motive power is required in comparison with the capacity of the mill, the hammers acting like fly-wheels. Any desired degree of fineness of division can be procured, since the material cannot escape from the mill except through the screens, which can be provided of various gauges.

Bauxite has also been converted into a kind of alum cake by the following method:—

Forty parts of powdered bauxite are mixed with 50 parts of 50° Bé. sulphuric acid and 10 of water. The mixture is heated gently, either in a reverberatory furnace or in lead-lined sheet-iron vats, and the aluminium sulphate sludge thus obtained is run into moulds where it sets very hard on cooling. This product has been utilised in the manufacture of paper of low quality.

89. **Purifying Aluminium Sulphate.**—The chief impurity to be eliminated is iron, the presence of which is highly objectionable in many instances. Its removal is an operation of great delicacy by reason of the similarity between the properties of the two metals, and has formed the subject of a number of inventions.

A. PRELIMINARY REMOVAL OF THE IRON IN THE MINERAL BY THE AID OF DILUTE ACIDS.—Attempts have been made to remove the ferric oxide present in bauxite, by treating the powdered mineral with dilute acids, and principally by oxalic acid, which readily dissolves this oxide. The result is, however, imperfect, even when the oxide has been previously reduced by heating in the presence of reducing gases.

B. TREATMENT OF THE SULPHATE LIQUOR WITH ZINC.—This process does not eliminate the iron, but simply transforms into ferrous sulphate the ferric sulphate present in the solution. It is, moreover, attended with the disadvantage of introducing zinc sulphate into the product.

C. SEPARATING THE ALUMINIUM IN THE FORM OF INSOLUBLE BASIC SULPHATE.—This method, proposed by Augé & Co., is based on the fact that if a suitable base, such as potash, soda, magnesia, alumina; or a salt, such as the carbonates of the above alkalis or magnesia, sodium aluminate, etc., whether hot or cold; be carefully added to a solution of aluminium sulphate containing iron sulphate, reduced by any means to the lowest stage of oxidation, the alumina will be sooner or later precipitated in the form of basic sulphates containing a large proportion of the sulphuric acid, whilst all the extraneous salts will remain in solution. It is then sufficient to wash the precipitate and add sulphuric acid, to obtain an aluminium sulphate of a high degree of purity.

According to the author's experience of this method, it seems to be a highly delicate one and not very practicable.

D. ELIMINATION OF IRON BY POTASSIUM FERROCYANIDE.—The ferrous liquors are diluted to about 20° Bé., and placed in wooden vats holding about 220 gallons, in which the iron is then thrown down as Prussian blue by means of potassium ferrocyanide (yellow prussiate) added as a hot solution until the precipitate ceases to increase—a condition recognised by testing small samples of the filtered liquor from time to time. If the end point has been exceeded, the surplus ferrocyanide is thrown down by a further quantity of the sulphate liquor.

After leaving the liquor at rest for about a fortnight, the clear portion is drawn off and evaporated. The Prussian blue precipitate is washed with water, filtered, pressed between felt, and sold. The quality is, however, inferior, and the blue is only fit for colouring common grades of paper. By treating the precipitate with sodium carbonate, it may be also converted into sodium ferrocyanide for use over again.

This process, although enabling the whole of the iron to be removed, and furnishing a very fine product in a simple and at first sight very economical manner, is really very expensive and not to be recommended, at least in some countries, since all depends on the rate of wages, the price of fuel and acid, and other considerations.

In fact, to enable the blue to settle down, it is necessary to greatly dilute the liquor, and consequently a large additional consumption of fuel is requisite for the evaporation process. Furthermore, the extremely slow rate at which the blue is deposited greatly retards the manufacturing process, unless the precipitation plant has been specially installed on a large scale for this process, it being necessary to leave the (20 Bé.) liquor for at least a fortnight after the addition of ferrocyanide, in order to give the precipitate time to subside.

The method has been carried on in England, coals and sulphuric acid being cheap; but would be unsuitable in France under the conditions prevailing there.

E. NEWLAND'S PROCESS.—Newland obtained a very pure product, containing only 0·082 per cent. of iron, by treating in a filter-press the evaporation products of solutions of crude aluminium sulphate. The iron remains in the mother liquors, and the products of the second operation are treated over again.

F. THE CHADWYK AND KYNASTON PROCESS.—In this process, which is worked in England, the liquor obtained by attacking bauxite is treated with arsenious acid to throw down the iron. The operation is completed by an addition of calcium ferrocyanide and zinc sulphate.

G. FAHLBERG'S PROCESS is based on the total precipitation of iron as a plumbate, when a ferrous solution of aluminium sulphate is treated with lead dioxide.

According to Pommier, the method of working is as follows:—

"The lead dioxide for this purpose is readily obtained by the reaction of 75 parts of 36° Bé. nitric acid on 100 parts of red lead (*minium*) in the cold. The resulting dioxide is of a brown colour, not black, the latter kind being a denser modification of the oxide and unsuitable for the purpose in view. Should the temperature of the operation be too high, this black oxide will be produced. The excess of nitric acid, together with the lead nitrate formed during the reaction, is removed by washing with water, and subsequent decantation. The work is carried on in clay vats.

"Another method easily applicable on the large scale, and preferably used by the inventors, consists in treating lead chlorite with a solution of bleaching powder. The lead chlorite is prepared, in the first place, by mixing 2 parts of litharge and 1 part of common salt in a mill, and grinding them in a little water or brine until the pasty mass has turned perfectly white. This mass, which consists of an alkaline basic lead chlorite, is transferred to an iron vat along with a concentrated solution of bleaching powder, and boiling is continued until the whole is of a brown colour, whereupon a slight excess of the bleaching powder is added. Finally, the mass is purified by a series of washings and decantations. It should be noted that the lead dioxide must be used in a moist state, and not dry, and for this reason it is employed in the pasty condition in which it is found after the washing process.

"The lead dioxide having been prepared by one of the methods just described, the next stage is performed in the same way as the ferrocyanide treatment. A predetermined quantity of the pasty dioxide is added to the cold solution of aluminium sulphate to be purified, whereupon the iron comes down as an insoluble, reddish-brown iron plumbate. Half an hour is sufficient for the complete separation of the iron. The proportion of dioxide required is naturally dependent on the quantity of iron present in the liquor, and is determined precisely by a series of tentative experiments. The ratio between the two is 20 parts of lead dioxide for each part of ferric oxide.

"It is necessary for the ferruginous solution to be in a basic or neutral condition, otherwise a portion of the lead dioxide would be attacked by the free sulphuric acid. The supernatant liquid may be separated from the precipitate by decantation after several days' rest, or at once by the aid of the filter-press.

"The purified solution is concentrated and cast in the usual manner. The iron plumbate is collected and treated for the recovery of lead dioxide, with which object it is mixed with sulphuric acid or nitric acid in a leaden vessel, to dissolve out the iron and leave lead dioxide behind. After syphoning away the solution of iron sulphate or nitrate, the traces of acid are removed by washing with water. Any unconverted lead dioxide which might have been present with the iron plumbate is recovered intact in this operation. The recovered lead dioxide may be used over and over again indefinitely, it being sufficient to make good the amount lost by washing.

"The cost of this process, which is employed in the works of Harrison Brothers & Co., Philadelphia, is 5s. per ton of aluminium sulphate containing 0·5 per cent. of iron."

Manganese dioxide behaves in a similar manner to lead dioxide; and stannic acid has also been recommended by Spence Glaser for the same purpose. A long time back, Persoz recommended the precipitation of ferric oxide by gelatinous aluminium hydroxide.

§ 2. ALUM MANUFACTURE

90. **Introduction.**—The name "alum" is generally applied in commerce to a double sulphate of aluminium with a base, such as potash, soda, ammonia, etc.

In ancient times the efflorescence of certain rocks supplied the Greeks, Romans, and Egyptians with a product known by the name of *alumen*, largely employed in medicine, dyeing, tanning, etc. According to Dioscorides and Pliny, several species of this product were known, some of them perfectly white, others more or less coloured, and all possessing a styptic flavour. They were all more or less complex mixtures of aluminium sulphate and iron sulphate, and the term *alumen* (from which the word alum is derived) had in those days a much wider significance than now.

Under the name of "glacial alumen," Geber described a substance which was obtained from Rocca in Mesopotamia (the modern Edesse, near Smyrna), and which was really an alum in the restricted sense of the term. Various other authors subsequently described bodies analogous to the alums, notably Paracelsus, who made use of the distinctive name "Rocca alumen," which has been corrupted into the French term "alun de roche" (rock alum).

The oldest method of preparing alum consisted in treating alunite or alum stone. This industry, which was of Oriental origin, was introduced into Europe about the thirteenth century, and the first important alum factory was established on the island of Ischia, towards the fifteenth century, by a Genoese merchant named Perdrix, who had travelled extensively in the East. The example was soon copied by Jean de Castro, another Genoese, who, struck by the resemblances existing between the rocks at Rocca and those at La Tolfa near Civita Vecchia, prospected for alunite, which he was not slow to discover. He then set up at La Tolfa an alum works, which afterwards attained great celebrity.

Finally, Antonio de Piena shortly afterwards founded a similar factory at Volterra, in the Grand Duchy of Tuscany.

In the seventeenth century a commencement was made with the manufacture of alum from alum earth in Hesse, Thuringia, and Saxony; but it was not introduced into England until the eighteenth century, during which period T. Chaloner set up the first alum works in Yorkshire.

Subsequently the method of preparing alum from aluminous and pyritic shales and lignites was elaborated in Germany and Picardy; whilst the process based on the direct union of alkali sulphates with aluminium sulphate obtained by treating clay, bauxite, cryolite, etc., is of comparatively recent origin.

The manufacture of alum has considerably declined in importance since the introduction of aluminium sulphate into commerce. Nevertheless, some 10,000 to 12,000 tons are still produced annually in France, the greater portion being obtained from alunite and pyritic lignites. This last-named method furnishes ammonium alum, and employs as a crystallising reagent sulphate of ammonia, which has been procurable at a very cheap rate for some years past.

Sodium alum, which until very recently was looked upon as merely a laboratory product, is at present manufactured in small quantities at several works, from aluminium sulphate obtained from bauxite. The two processes most in use are those of Augé and Kessler, descriptions of which are given below from the patent specifications of the inventors.

We will now proceed to describe the various methods that have been in use or are still employed for the preparation of alum, laying most stress on the treatment of alunite and pyritic lignites.

91. **Manufacture of Alum from Clay, Kaolin, Bauxite, etc., Sodium Alum.**—*A.* ORDINARY ALUM.—The first stage of the process is invariably the preparation of a liquor rich in aluminium sulphate. This is effected by methods already described, and therefore need not be repeated.

The liquor is heated up again and mixed with the requisite quantity of potassium sulphate, potassium chloride, or ammonium sulphate; and as soon as the added salt is dissolved the hot liquor is run into the crystallising pans, where the alum crystallises out. To convert this alum into a merchantable form it must be re-crystallised.

The mother liquors obtained in this process are very troublesome, and their concentration is a very important operation, since it ensures the recovery of the excess of sulphuric acid from the initial stage, as well as a somewhat considerable quantity of alum. With this object the mother liquors and washings are run into lead-lined wooden vats, and concentrated by steam heat to 40° Bé., the resulting hot lye being mixed with a suitable quantity of sulphuric acid and used over again for attacking the alum mineral employed. By proceeding in this manner none of the mother liquor is wasted, which is an important consideration. On the other hand, when a ferruginous mineral is employed, the iron continues to accumulate in the mother liquor to such an extent as to eventually render the latter unfit for use.

J. Wiernick (*Zeitschrift für angewandte Chemie*, May 15, 1894; *Moniteur Scientifique*, 1895, p. 221), however, has shown that the mother liquor can be freed from iron in a very simple manner by effecting the concentration under special conditions. In fact he states that if the concentration be continued to 50° Bé. instead of 40° Bé., a deposit of an iron salt, the composition of which varies according to the conditions of the operation, is formed in the concentrators. This precipitate separates very quickly, leaving a clear liquor almost entirely free from iron and fit for use over again.

The following analyses show the progressive diminution in the iron content as the concentration of the liquor increases:—

	Bé.		Fe per litre.
Mother liquor at	30°	contains	16·80 grms.
,, evaporated to	42°	,,	13·20 ,,
,, ,,	45°	,,	11·56 ,,
,, ,,	47°	,,	8·80 ,,
,, ,,	49°	,,	8·04 ,,

The composition of the precipitate requires to be carefully watched, as it varies according to the state of oxidation of the iron in the liquor. With liquors that have been fully oxidised, the precipitate is yellowish white, crystalline, and insoluble in water; and it readily forms incrustations on the steam coil in the concentrating vessel, thus preventing the transmission of heat. Furthermore, it causes a loss of alumina and potash, or ammonia, the yellow insoluble mass formed containing the sulphates of these bodies in addition to iron sulphate.

When washed, dried, and analysed, this precipitate has been found to contain

	(I.)	(II.)
Fe_2O_3	23·88	23·02
SO_3	53·90	58·77
Al_2O_3	7·25	7·50
NH_3	2·36	2·40
K_2O	7·06	6·92

and therefore consists of a basic salt corresponding nearly to the formula

$$2Fe_2O_3, 5SO_3, Al_2(SO_4)_3, K_2SO_4, (NH_4)_2SO_4,$$

the exact equivalent of which is represented by the composition—

Fe_2O_3	23·37	NH_3	2·48
SO_3	58·48	K_2O	6·86
Al_2O_3	7·52		

It being desirable to prevent as far as possible the formation of this compound, it is necessary to reduce the ferric salts to the ferrous state, and for this purpose Wiernick finds shavings of green poplar wood form a very suitable reducing agent.

If, after these shavings have been placed in the vat, the concentration of the liquor be continued to about 50° Bé., the greater part of the iron is deposited as an amorphous black mass consisting exclusively of iron salts, as shown by the following analytical data:—

	(I.)	(II.)
FeO	16·98	17·20
Fe_2O_3	25·76	28·48
SO_3	57·68	57·22

which figures agree very closely with the formula

$$3Fe_3O_4, 2Fe_2(SO_4)_3.$$

The foregoing method of purification is said to have yielded very satisfactory results.

B. SODIUM ALUM.—I. *Introductory Remarks.*—In the same manner as aluminium sulphate forms alums with the sulphates of potassium and ammonium, it also furnishes with sodium sulphate a product known as sodium alum, Na_2SO_4, $Al_2(SO_4)_3$, $24H_2O$, a body differing, however, from the others by its ready solubility in water (110 parts per cent.).

From the industrial point of view, the chief importance of this property is the difficulty that thereby arises in the separation of sodium alum from other salts in solution, notably iron sulphate; and it is this consideration that has prevented the extension of the sodium alum industry, notwithstanding the relatively very low price of sodium sulphate in comparison with the corresponding potassium and ammonium salts.

For the manufacture of sodium alum a comparatively pure raw material, such as bauxite, is absolutely essential; and hence the whole process may be regarded as the reverse of sensible, from an industrial point of view, since the direct conversion of bauxite into aluminium sulphate gives a product richer in alumina than is the final product aimed at (sodium alum), and one sufficiently pure for most purposes.

Nevertheless, in certain cases, and by working under well defined conditions, the crystallisation of sodium alum may be managed so that the mother liquor removes a portion of the impurities, a product of sufficient purity for certain delicate applications being thus obtained. In this case the manufacture of sodium alum becomes a matter of interest, in view of the cheapness of the crystallising reagent.

Even when working with pure materials the manufacture of sodium alum is a very delicate operation, the affinity of sodium sulphate for aluminium sulphate being comparatively feeble and their union to form alum accomplished with difficulty—in fact, only complete under certain well defined conditions. Thus by cooling down to a low temperature (in winter) a mixture of equivalent proportions of aluminium sulphate and sodium sulphate, in solution, the author has obtained a mixture of sodium alum with a larger or smaller quantity of sodium sulphate, instead of the crystallised alum alone.

Moreover, even highly concentrated solutions of sodium alum have a great tendency to become supersaturated, and crystallise with great difficulty. A highly concentrated solution when quite cold will become turbid immediately, and deposit crystals on decantation or agitation. These phenomena of supersaturation become more and more accentuated as the degree of impurity of the solution increases.

The process of solution of sodium alum in water exhibits certain interesting peculiarities.

Thus, if the alum crystals be heated very briskly in water they subside into a pasty white mass, which, notwithstanding the ready solubility of this compound in water, becomes disseminated throughout the liquid, and forms a very thick milky emulsion. Even when the proportion of water is large, the solution often remains opalescent and exhibits nacreous striations.

Here we are evidently in presence of a phenomenon of dehydration within the bosom of the liquid, a peculiarity observed in the case of other salts, especially ferrous sulphate, but to a particularly remarkable degree in the instance now under consideration.

Remarkable peculiarities are also exhibited in the crystallisation of this alum. In one experiment sodium alum was dissolved in distilled water, and the solution concentrated to 39° Bé. When cooled the liquid solidified to a white mass, the surface of which was found next day to be covered with beautiful flattened triangular crystals representing a modification of the octahedron, the sides of some of them measuring up to 1 cm. With a view to re-dissolving the mass it was then sprinkled with a little water and stirred with the thermometer, whereupon, to the author's surprise, crystallisation proceeded rapidly, accompanied by a rise in temperature, until finally the capsule contained a large number of well formed transparent crystals of sodium alum, together with a mother liquor in which nearly all the iron of the solution was retained.

Curiously enough, these observations, made incidentally by the author in the course of experiments on the manufacture of sodium alum, had already—as was subsequently ascertained—been utilised industrially by Augé and Kessler, brief abstracts of whose patent specifications are given below.

At the present time sodium alum occupies a certain position in the industrial world, though the output, which a few years back appeared likely to threaten that of the other alums, has now become stationary. It is chiefly employed in paper-making, and is besides, in virtue of its great solubility, more convenient in application than either potassium alum or ammonium alum.

II. *The Augé Process.*—In this process a solution of sodium sulphate is mixed with one of aluminium sulphate, and the whole concentrated to 39°–40° Bé. The resulting paste is then spread out on inclined leaden plates, so as to allow the mother liquor (forming about ¼ of the total weight) to drain off. The temperature is maintained at about 10° or 15° C. during the period of crystallisation. The mother liquor removes almost the whole of the impurities.

The temperature has an important influence on the percentage of alumina in the alum; and, in fact, if the crystallisation be effected at about zero, only 7 per cent. of alumina is present in the product.

The author has examined the alum furnished by this process. It is in the form of small, highly efflorescent, exceedingly white crystals, which assume but a very slight bluish coloration when tested with ferrocyanide. It is probable, however, that this low content of iron is due more to the extreme purity of the materials employed than to the method of preparation.

III. *The Kessler Process.*—Several methods of obtaining sodium alum have been patented by this inventor.

One of them consists in concentrating a solution of the two sulphates so as to obtain a pasty mass, as in the Augé process. This paste is then mixed with a sufficient quantity of the water drained from a previous batch, and a number of crystals are added to serve as nuclei for the crystallisation which then ensues. The iron remains in the mother liquor.

Another method is to prepare a concentrated solution of aluminium sulphate (53° Bé., measured at boiling temperature), which is then cooled until just on the point of setting, whereupon it is mixed with sufficient mother liquor from a previous batch to form a liquid measuring very little more than 40° Bé. (at 40° to 50° C.) after adding sodium sulphate equivalent to 40 per cent. by weight of the aluminium sulphate taken.

Finally, a third process consists in adding to mother liquor or water alternate solutions (more or less concentrated) of the two sulphates, in the proportion of 40 parts of sodium sulphate per 100 of aluminium sulphate (53° Bé. strength at boiling temperature), so that the liquid finally measures no more than 40° Bé. at 45° C., the solution being left to crystallise after each addition.

In his patent specification Kessler describes the various operations in the following manner:—

The solution of sodium alum is evaporated to 45° Bé. strength and cooled down to 16° or 22° C. It first sets to a pasty mass which crystallises spontaneously in transparent crystals, the operation being, however, accelerated if a few crystals are dropped in.

In the summer time a 40° to 50° Bé. solution of sodium alum may be poured, even boiling hot, over ready formed crystals of the same alum impregnated with the mother liquor, and neither turbidity nor magma will be formed, provided the mixture is stirred and incorporated quickly. Assistance is afforded in this respect by the reduction in temperature resulting from the liquefaction of the crystals. The operation is arrested before the appearance of a turbidity, which would occur at about 40° or if the mixture has not been effected with sufficient rapidity. When the temperature reaches 22° to 23° C. the solution is poured into vats, where it sets completely.

The procedure may be modified by introducing sodium sulphate crystals, reduced to very fine powder, into the aluminium sulphate solution.

To prepare the alum solution, sodium bisulphate may be used, the salt being dissolved in 45° or 60° Bé. sulphuric acid, and the resulting solution employed for attacking the aluminous mineral.

Again, the sodium bisulphate may be dissolved in aluminium sulphate solution, the result being to liberate sulphuric acid, which may be utilised as a solvent for the calcination products of the mother liquors from several crystallisations. The sodium sulphate introduced is recovered by sufficiently diluting the alum solution and cooling it down to 10° C., whereupon the excess of sodium sulphate crystallises out, leaving the alum behind in solution.

A small sample of Kessler's sodium alum, preserved in the author's laboratory, is in the form of larger and harder crystals than those from the Augé process; they are also more transparent and less efflorescent. On the other hand, the colour is somewhat inferior, having a very pale violet-yellow tinge. In contact with ferrocyanide they exhibit a strong blue coloration, and therefore contain a notable proportion of iron.

92. **Manufacture of Alum by the Spence Process.**—This is a very old method, dating back to 1845, and one that has been largely employed.

The raw material used is a black clay (shale), forming an extensive vein, situated directly under the true coal bed in the Lancashire basin. This clay is combustible on account of its large content of organic matter.

The raw material is first burned in heaps, from 40 to 80 inches high, which are replenished in proportion as they subside. The operation of roasting takes about 10 days, and when properly carried out—at a temperature not exceeding dull red heat—yields a reddish, friable, and porous residue. This residue is then placed in large open tanks heated from below, and treated with 34° Bé. sulphuric acid, the temperature being maintained at about 110° C. Each charge consists of about 20 tons of mineral. Whilst the formation of aluminium sulphate is in progress, and the temperature is at the level indicated, a current of ammoniacal vapour, from a distilling apparatus or from the ammonia water of gas works, is blown into the tanks, the quantity admitted being carefully regulated so that a large excess of sulphuric acid is always present. The liquor in the tanks is thus gradually converted into a concentrated solution of ammonium alum, and, when sufficiently clarified by repose, is drawn off into crystallising pans, where the alum is precipitated by rapid cooling and continued agitation. The alum powder thus obtained is drained and washed with a saturated aqueous solution of alum.

The product is entirely free from iron, but has to be brought into a merchantable condition by re-dissolving it with steam and running the solution into lead-lined wooden moulds, where the alum crystallises in blocks which are chipped out with axes.

On the average, about 15 cwt. of the black clay are needed to produce 1 ton of ammonium alum. Spence also subjected aluminium phosphate to a similar treatment for the preparation of the same product.

93. **Production of Alum from Natural Felspar.**—At the present day no interest attaches to the methods proposed for utilising these materials: a few words may, nevertheless, be devoted to the manner in which attempts have been made to recover the alumina and potash in felspar for the manufacture of alum.

Mohr recommended the mixing of 130 parts of felspar with 70 or 88 parts of potassium carbonate, sufficient water being added to form a plastic paste. The mass was divided into briquettes, and, after being calcined moderately, moistened with water, and treated with 196 parts of concentrated sulphuric acid, furnished a solution of alum and a residue of silica.

Turner proposed to fuse felspar with potassium sulphate, and incorporate the molten mass with potassium carbonate. The vitreous mass, when treated with water, parts with its soluble potassium silicate and leaves a residue which, on being treated with boiling sulphuric acid, furnishes alum and silica.

Another proposition was to react with sulphuric acid on a mixture of 2 parts of felspar and 3 of fluorspar, the mass being kept at red heat until the disengagement of hydrofluoric acid vapour ceased. The residual mass yielded alum when extracted with water.

94. **Treatment of Alunite. Joint Production of Alum and Aluminium Sulphate.**—Alunite, as a mineral product, has already been dealt with on an earlier page, so we may now proceed at once to the methods of treatment to which this body is exposed.

A. THE LA TOLFA PROCESS.—The mineral, broken in lumps the size of paving setts, is subjected to a very simple method of treatment, consisting in roasting the lumps in heaps or in kilns. The operation requires to be very carefully performed, it being necessary to avoid an excessively high temperature, which would decompose the aluminium sulphate and liberate sulphur trioxide and dioxide. When such liberation begins—manifested by the appearance of dense white acid fumes—the operation is stopped, and the roasted mass transferred to brickwork bins, where it is left to effloresce for 3 or 4 months, with occasional waterings. At the end of that time the whole will have become in a measure slaked, and is then lixiviated to extract the alum. The liquor is concentrated and run into the crystallising pans, where the alum crystallises out; but as the liquor contains in suspension a kind of rose-red mud, rich in ferric oxide, the alum crystals are tinged with the same colour.

This alum crystallises in cubes and not in the ordinary octahedral form. It constitutes the Roman alum so highly prized by consumers on account of its freedom from soluble compounds of iron.

B. THE POMMIER PROCESS.—Messieurs Pommier treated Madriat alunite for the purpose of obtaining alum and aluminium sulphate at the same time.

The following is the method employed (Pommier's article on Aluminium Sulphate and Alum, in Fremy's *Encyclopédie*):—

"The alunite is first reduced to a very fine powder in a mill fitted with heavy cast-iron runners and with a collector which scrapes the ground mineral on to a shaking sieve. After this it is calcined in a reverberatory furnace with a flattened arch, at a temperature not exceeding dull red heat, as otherwise a portion of the sulphuric acid in the alunite is decomposed. At the end of about 2 hours the charge is drawn from the furnace and placed in an iron box, from which it is transferred to a cast-iron pan about 60 inches in diameter, set in the ground so that only about 12 inches project above the surface. Here it is treated with 35° Bé. sulphuric acid, previously heated in a small leaden boiler, the quantity being regulated so that 525 parts by weight of acid are used to 400 parts (original weight) of alunite. A violent reaction ensues and is quickly terminated, the mass being meanwhile kept stirred with large iron paddles to ensure uniformity of action throughout.

"The mass then quickly sets hard and is divided, by long iron tools with cutting edges, into manageable pieces which are loaded on open trucks of sheet-iron. The loaded trucks are run on rails into a furnace heated to a low temperature by means of coal or (better) coke, and consisting of a low brickwork chamber built on the ground and closed by a cast-iron door, the hearth being at the opposite end. The object of this operation is to complete the attack by several hours' exposure to moderate heat, the brief duration of the violent reaction being insufficient to attain this result. On leaving this furnace the lumps of crude product are spread out on flat ground covered by shed roofs, where they are left for several weeks, it having been found that the reaction still continues and becomes completed thereby, so that even the hardest lumps are finally disintegrated and converted into dust. Then follows the process of lixiviation in a cylindrical leaden pan heated by direct steam. When all the soluble matters have been extracted by the water the mass is left at rest for about 48 hours; the insoluble portion, largely consisting of silica, is deposited, and the clear liquid, which is nothing more than a solution of alum and aluminium sulphate, is decanted. The density of this solution is between 20° and 25° Bé., and is increased to 30° Bé. by evaporation in a concentrating pan, whereupon the liquor is poured out into a rectangular leaden vat holding about 4500 gallons, on the walls and bottom of which the alum crystallises out on cooling. After the lapse of a week or 10 days the mother liquor (a solution of aluminium sulphate) is syphoned off, concentrated (generally to about 50°), and run into a crystalliser in the usual manner.

"As for the alum, that portion which settles on the walls of the vat consists of small true octahedral crystals, which are readily separable and form the commercial 'granulated alum,' which is ready for sale as soon as it has been drained. On the other hand, the portion deposited at the bottom (the bulk) is in the state of a fine crystalline powder, retaining some of the mother liquor and forming an unsaleable, dirty, wet paste, which has to be re-crystallised to bring it into a merchantable condition."

C. METHOD NOW IN USE.—I. *Preparation of the Mineral.*—The process now to be described is the one in most general use at the present time, those mentioned above being of little more than historical interest.

The mineral employed in France is derived from the deposits at La Tolfa in Italy, those in Auvergne being neglected for some reason unknown to the author.

The average composition of the crude, sifted La Tolfa alunite, utilised in the manufacture of alum and aluminium sulphate, is—

Alumina	23·50–29·00 per cent.
Iron oxide	2·00 ,,
Sulphuric acid	16·30–20·00 ,,
Potassium sulphate . . .	10·00–14·00 ,,
Insoluble in HCl	17·40 ,,
Loss at low red heat . . .	35·80 ,,

The lump alunite is finely powdered by the aid of mills similar to those already described in dealing with the treatment of bauxite, and is then roasted in a reverberatory furnace with a flattened arch (Figs. 111, 112), the mineral being spread on the bed to a depth of 4 to 6 inches. The temperature employed is equal to about the fusing point of copper, and the operation results in a loss of weight, varying in accordance with the composition of the mineral and the manner of roasting, but averaging about 33 per cent.

The roasted material has the following mean composition:—

Loss at dull red heat .	4·30 per cent.	Iron oxide . . .	3·08 per cent.
Insoluble in H_2SO_4 .	26·20 ,,	Sulphur trioxide . .	24·40 ,,
Alumina . . .	34·92 ,,	Potash . . .	7·50 ,,

II. *Attacking the Mineral.*—The apparatus used is the same as in the case of bauxite, and the operation is conducted in a similar manner, with certain modifications necessitated by the nature of the material and greatly influencing the purity of the product.

In crude alunite the iron is present for the most part in the form of ferrous compounds, and the operation of roasting, far from raising this iron to a higher stage of oxidation, tends to minimise the proportion of ferric compounds, chiefly by reason of the reducing action of the sulphur dioxide formed.

In the chemical treatment the peroxidation of the iron by means of oxidising agents is one of the principal aims in view, the ferric sulphate thus formed being eliminated from the liquor, either as an insoluble iron alum or as basic sulphate, by a simple manipulation during the subsequent treatment. Contrary to what happens in the case of bauxite, the solutions obtained from alunite are thereby considerably purified, the results, though generally imperfect, being none the less of great importance.

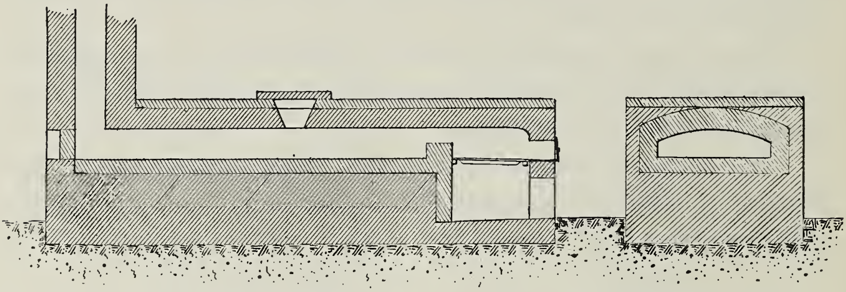


FIG. 111.—Longitudinal section. FIG. 112.—Transverse section.

Reverberatory furnace for roasting alunite.

In considering the method of conducting this chemical treatment, let us take, for example, the case of the trunco-conical vessel described in connection with bauxite—

The cubical capacity of the truncated cone is	5·200 cub. m.
,, ,, cylinder ,,	24·500 ,,
Total	29·700 cub. m.

For a vessel of this capacity, about 30 cub. m. (6600 galls.), the charge of alunite will amount to 8 tons and the acid to 4 tons, calculated as SO_3. This sulphuric acid is introduced in the state of acid liquors from previous operations and containing 300 to 350 grms. of SO_3 per litre, the volume of 35° to 40° Bé. liquor being therefore about 2500 gallons. Directly the acid liquor is run in, the steam and air taps are turned full on, the charge of roasted alunite is admitted, 2·2 lbs. of sodium nitrate per ton of material (17½ to 22 lbs. altogether) being added at the same time.

When the reaction is terminated (*i.e.* the liquor obtained is neutral), which generally takes about 2 or 3 hours, a solution of chloride of lime is introduced into the mass in order to complete the peroxidation of the iron, the proportion of chloride of lime required being usually about 3·3 lbs. per ton of alunite (*i.e.* about 26½ lbs.). Water is then immediately added to dilute the solution to about 30° to 35° Bé., the steam is shut off, and only the Körting injector kept going, in order to keep the temperature of the mass as near 80° C. as possible. It is at this stage that the purification of the liquor goes on, and the longer the temperature of 80° C. is maintained the better is this cleansing effected.

This heating process is continued for 20 to 30 hours to produce "superior" aluminium sulphate, while for the "purified" quality it is necessary to keep the temperature at 80° C. for 120 hours. If this condition of temperature is not accurately maintained, the purification will oftentimes be imperfect and the liquor become acid again. In such event the method is being improperly conducted. A general rule for the production of neutral liquor is to employ a very strong and highly acid liquor for the reaction, the temperature being then higher at the outset and the attack proceeding more rapidly and completely. It is also necessary that a rapid fall in temperature should occur as soon as the concentration of the liquor increases, the temperature being reduced to 80° C. as quickly as possible, and never allowed to rise again. In this event the final liquor should remain neutral.

The liquor will exhibit a density of about 32° Bé., and a degree of acidity varying with the accuracy of performance attained. It is then left to clarify, which it will do in less time than is required for bauxite, and is decanted as soon as possible, for removal to the crystallising plant. A high temperature should prevail during decantation, in order that the whole of the alum present may be retained in solution. The residue is lightly washed, and, the washings being decanted after dilution to 20° to 25° Bé., the remaining mass is treated with acid, an operation requiring great care in order to produce the best results.

For this purpose about 10 tons of pure 52° Bé. sulphuric acid are run in, and followed, whilst the application of heat is still proceeding, by a further (gradual) addition of 6 tons of 52° Bé. acid in the form of acid sulphatic solutions of 40° Bé. density, and containing 300 to 360 grms. of SO_3 per litre, the total acid being equivalent to 1 part of SO_3 (0·6 in the pure state and 0·4 as acid liquor) per 1 part of mineral. About 10 to 12 hours are required for this operation, during which time the application of heat and the injection of air are continued without interruption, and a variable quantity of acid sulphatic liquor——measuring 40° to 41° Bé. density, and containing an average of 350 grms. of SO_3 per litre—is obtained. In the case under consideration the volume of liquor is 4400–5000 gallons.

As soon as this liquor has been run off, the residue is washed with weak (5° to 10° Bé.) liquor, and removed to leaden tanks where it is washed with water, the whole of the washing liquors being employed again in the cycle of operations.

The total length of time occupied by the treatment is about 80 hours in the case of the "superior" quality of product, but much longer for the "purified" aluminium sulphate, in consequence of the prolonged exposure at 80° C. then necessary. Other considerations, such as the nature of the mineral, the duration of the attack, the conditions of decantation, etc., also influence the time taken up by the process.

The progress of the purification is controlled by tests for the iron, and the precipitation of the latter can also be checked by colorimetric tests with ferrocyanide or thiocyanate. For controlling the progress of the attack, recourse is had to the Baumé areometer, acidimetric titration of the liquor, and analysis of the residues.

In working with the rectangular vats described in dealing with bauxite, the progress of the attack, etc., is the same as already defined. In any case, endeavours are made to restrict the consumption of sulphuric acid to 100 parts of 60° Bé. acid per 100 parts of mineral, for the production of inferior grades, and to 90 parts for neutral alum, though these figures are always slightly exceeded in practice. About 120 to 130 per cent. of sulphuric acid represents the average consumption in attacking the alunite, *i.e.* a loss of 20 to 25 per cent. of acid, either left in the residues or carried away as free acid in the inferior grades of alum. The outlay involved is a variable quantity, and is least when trunco-conical vats are employed and the residue is properly exhausted.

The residue, calcined after washing, should contain 90 per cent. of matters insoluble in hydrochloric acid, and 1·4 to 1·5 per cent. of alumina and iron oxide. When trunco-conical vats are used, the residue, merely dried at 100° C. without calcination, contains 87 to 90 per cent. of insoluble matter, and 3·75 per cent., at most, of iron oxide and alumina; whereas with rectangular vats the insoluble matter in the residue amounts to only 75 per cent., whilst the iron oxide and alumina attain to 7 and even 14 per cent., thus representing a considerable nett loss.

The efficient performance of the work greatly depends on the men in charge of the operations, since on their carefulness hangs the neutrality of the products and the proper exhaustion of the residues. As a general principle the quantity of alumina escaping attack should be reduced to a minimum, as well as the quantity of free acid in the liquors destined for the production of neutral sulphate, the final excess being saturated with pure alumina at the stage of concentration.

In order to obtain good results in these respects a system of premiums and fines, given or levied as the work is well or ill done, is of use in stimulating the men and inducing them to look properly after their duties.

III. *Crystallising and Purifying the Alum.*—As we have seen, the liquors resulting from the acid treatment of the mineral are delivered to the crystallisers. These vessels differ in various works. Sometimes they are large brick tanks lined with lead and embedded in the ground; but this system is very expensive, and is inconvenient on account of the difficulty in discovering leakages. The crystallisers used in Lacarrière's works at Noyon are of a much more efficient type, being made of wood lined with thin sheet-lead, and slightly raised above the level of the ground, thus enabling leaks to be at once detected, and increasing the rate of cooling.

The alum crystallises on the walls of the pans, and, when the temperature is sufficiently reduced, the mother liquor is drawn off and sent to be concentrated, whilst the alum itself is broken out and re-crystallised to bring it into merchantable condition. With this object the crude alum is placed in a copper or leaden cylinder into which steam is introduced as required, and produces a concentrated solution of alum, of the density 40° to 42° Bé. at boiling temperature. After leaving the solution for an hour, to allow the insoluble matter to settle down, it is syphoned off into leaden moulds of a cubical capacity of 70 to 90 cubic feet.

The moulds are made of two or three breadths of plank covered on the inner side with thin sheet-lead, the lateral joints being packed with sheet-caoutchouc and tightened with nuts and screws, whilst the joint against the boarded floor is luted all round with clay. The alum crystallises to a depth of 10 to 12 inches all round the interior of the mould. After about a fortnight the moulds are taken to pieces, the blocks of alum are broken to allow the mother liquor to drain away, and the lower part of each block is cut away with axes, being impure and contaminated with the clay luting, and requiring purification by a second re-crystallisation. The remainder is formed into solid transparent blocks and sold in that condition, or else broken into lumps about the size of the fist and packed in bags or casks. These operations will be described later on in dealing with the treatment of lignites. Sometimes the alum is desired in a pulverulent form, and in such case the 40° to 42° Bé. solution is poured into ordinary crystallising pans, so as to be cooled at a more rapid rate than in leaden moulds, the liquid being kept stirred all the time. The resulting finely divided flour of alum is freed from the accompanying mother liquor in a centrifugal separator, like those used in sugar works, but lined with lead, the alum being discharged in an almost dry, pure condition.

The re-crystallised alum invariably gives a slight blue colour reaction with ferrocyanide, and, if desired perfectly pure, must be again crystallised in the same manner as before.

Occasionally a demand arises for alum in the form of coarse powder. This may be produced by grinding the crystals in mills, which will form the subject of description later on.

IV. *Concentrating Liquors for Aluminium Sulphate, and Handling the Product.*—The mother liquors from the alum crystallisers are concentrated in the manner already described in dealing with bauxite. It is always advisable to have the liquor for concentration of as high a density as possible, since by this means the loss of alum, by retention in solution, is reduced to a minimum, and less fuel is required for the concentration process. The most suitable density for the liquor is 35° Bé. in summer and 34° Bé. in winter, and this strength should be attained in the crystallisers.

The different grades of aluminium sulphate and degrees of concentration required for their production have already been discussed, and need not be gone into again, except to mention that for purified sulphate, very rich in alumina and low in iron, the liquor is concentrated to 60°–62° Bé. and poured on to copper plates. The product from alunite is handled in the same way as that from bauxite, and it is therefore unnecessary to describe the various operations again.

It will be apparent that, apart from the mixed production of alum and aluminium sulphate, the principal differences in the treatment of alunite and bauxite are, that the one mineral needs roasting whilst the other does not; secondly, the liquors from alunite require treating with oxidising agents, a superfluous measure in the case of bauxite. The main divergence between them, however, so far as the final results are concerned, is that in the one case the purification is effected spontaneously under slightly different conditions of attack, thus enabling products of a high degree of purity to be obtained, whereas from the other none but inferior grades can be procured. It may be that this purification is effected by the heat in presence of an excess of unattacked material, the alumina of which, under the influence of time, replaces iron in the solution. It would therefore be interesting to ascertain whether an analogous result could be obtained by adding to bauxite an excess of some readily attackable aluminous compound.

A ton of alunite furnishes about 14 to 16 cwt. of alum, sometimes more, and about 2 tons of aluminium sulphate containing 15 per cent. of Al_2O_3.

The subjoined figures give the composition of several grades of aluminium sulphate:—

	Ordinary concentrated to 46° Bé.	Neutral concentrated to 56° Bé.	Retrograde or superior.
Total SO_3	33·27	36·50	37·00
Al_2O_3	11·78	14·36	15·10
Fe_2O_3	1·42	1·14	0·30
Loss on calcination	60·50	48·10	48·10
Free SO_3	8·60	0·00	0·00

95. **Production of Alum from Pyritic Shales or Lignites.**—This operation entailing the conjoint production of alum and ferrous sulphate, this interesting industry will be dealt with after the various methods of preparing the last-named salt.

CHAPTER IV

The Manufacture of Sulphates of Iron

§ I. FERROUS SULPHATE

96. **Introduction.** — Ferrous sulphate, also named green vitriol or green copperas, has been known for a very long time, and is indeed one of the most important salts of iron. Formerly its uses were restricted, and it did not make any headway until the discovery of its possibilities in connection with the production of Nordhausen sulphuric acid on a manufacturing scale. At a later date considerable quantities were consumed in the manufacture of coal gas, in dyeing, and in disinfecting; and though at present its use in the dyeing industry has fallen away into insignificance, agriculture, on the other hand, affords a large and increasing outlet for ferrous sulphate, in consequence of new discoveries of its utility, *e.g.*, in connection with the treatment of chlorosis in the vine, the destruction of wild mustard (*sinapis arvense*), etc.

Strictly speaking, the manufacture of ferrous sulphate does not constitute an industry at all. In some cases its production is of a secondary and occasional nature, being pursued or abandoned in accordance with the state of the market and the commercial value of the product; whilst in certain industries it is obtained as a bye-product in the manufacture of other substances, seldom of an allied character. Under the latter circumstances, ferrous sulphate often forms an inconvenient residue which the maker is glad to get rid of at any price. Thus in the metallurgy of copper, the pickling of sheet-iron, cleaning white iron, galvano-plastic operations, and the treatment of pyritic shales and lignites, large quantities of this salt are produced.

Other manufacturers, in order to utilise certain acid or metallic residues of low value and difficult sale, occasionally go in for making ferrous sulphate, notwithstanding its low price. Petroleum refiners, for example, utilise in this way the acid tar (sludge acid) obtained in refining and containing up to 50 per cent., by weight, of SO_3. Similarly, the waste accumulating in the wire-drawing industry is occasionally utilised, on the spot, for making ferrous sulphate. On account of the different methods employed in the preparation, commercial ferrous sulphate may contain highly divergent impurities, such as copper, zinc, lead, alumina, lime, magnesia, etc. As this variety cannot fail to possess a certain amount of interest, the principal methods of producing this salt will now be described.

97. **Preparation from Pyrites.**—In addition to the minerals utilised for the manufacture of alum, certain natural sulphides of iron, such as the different varieties of pyrites, are treated for the production of ferrous sulphate. This treatment is identical with that employed for the alum minerals, and which will be described later on.

Pyrites is piled in large heaps on a flat surface, previously puddled with clay, where it is subjected to efflorescence and roasting, *i.e.* conversion from the state of sulphide into that of a sulphate, under the influence of moisture and atmospheric oxygen. The arrangement of this roasting place is such as to facilitate the collection and storage, in a suitable reservoir, of the liquor resulting from the lixiviation of the heaps by running water or water pumped over them. The liquor collecting in the reservoir is repeatedly pumped over the heaps, in order to ensure its progressive enrichment. When a given strength is attained the liquor is left to settle and clarify, is then concentrated by evaporation, and drawn off to be crystallised. The salt thus obtained is invariably aluminous.

Occasionally, in certain localities, pyrites is found which has oxidised spontaneously, and which may therefore be used direct for the manufacture of ferrous sulphate without having to pass through the stages of roasting and efflorescence.

Another mode of dealing with pyrites with a view to the production of ferrous sulphate is intimately connected with the manufacture of sulphur. In this case the pyrites is distilled in clay retorts similar to those used in gas works, but smaller, holding a charge of not more than 65 lbs. Under the influence of heat the pyrites decomposes and liberates sulphur, which is condensed in chambers. At the end of 6 hours distillation may be considered complete, and about 19 per cent. of sulphur will have been obtained, the quantity remaining in the residue being about double that distilling over. This residue forms a highly suitable material for the production of ferrous sulphate. It is thrown into heaps in admixture with the residue from a previous lixiviation, and oxidation is started by setting fire to a layer of wood under the heap, the process then continuing automatically. After about a year the mass is ready for extraction. This operation is carried out in large flat basins, where the roasted mineral is sprinkled with water, the resulting solution, which has a density of about 20° Bé., being drawn off, left to clarify, and evaporated. When concentrated to about 41° Bé. the liquor is run into crystallising pans.

The residue from this process contains a large proportion of ferric oxide, basic ferric sulphate, and impurities. Part of it is used in the manufacture of colcothar, and the remainder is mixed with the still residue and roasted over again.

98. **The Spence Method.**—This method was designed to utilise the residue from roasted pyrites used in the manufacture of sulphuric acid. It is necessary that the pyrites should be less highly roasted, and should retain a larger proportion of sulphur than usual in the sulphuric acid process, the residues from which are mainly composed of ferric oxide.

To prepare ferrous sulphate from a residue of this kind, Spence digested it with dilute sulphuric acid (about 22 per cent. Bé.), and obtained in about 12 hours' time a liquor of about 33° Bé., which he concentrated and crystallised. The reaction of sulphuric acid on the residue was accompanied by a slight disengagement of sulphuretted hydrogen. The undissolved mass was treated over again with sulphuric acid, and the process repeated until a residue, very rich in sulphur, was obtained suitable for use in the manufacture of the sulphur dioxide required for the work of the leaden chamber.

Other methods have been proposed for utilising pyritic residues. Négrier, in particular (French Pat. 217,602, Nov. 27, 1891), proposed to heat the residue to 100° C., and pass over it a current of sulphur dioxide and steam, the reaction being accompanied by an elevation of temperature up to 250° C.

99. **Preparation of Ferrous Sulphate from Native Ores.**—This process, which was first employed by Janicot in the preparation of a ferrous sulphate, utilised in dyeing at Lyons and St. Etienne, consists in dissolving in 40° Bé. sulphuric acid certain native iron ores, such as spathic iron—which for the most part is composed of ferrous carbonate associated with carbonates of lime and manganese, together with silica, clay, etc. When the reaction is finished the mass is left to settle, the liquid is poured off, and leaves behind a residue of carbonaceous matter, clay, calcium sulphate, etc.

This process may also be applied to minerals comparatively rich in chalk, provided they are previously treated with dilute (4° Bé.) hydrochloric acid, which merely dissolves the carbonates of lime and magnesia without attacking the carbonate of iron. The residue is then treated with sulphuric acid as already described.

100. **Preparation of Ferrous Sulphate from Metallic Iron and Sulphuric Acid.**—The ferrous sulphate obtained by this process is exceedingly pure, and meets with a ready sale. It being uneconomical to employ materials of good quality for this purpose, the residues from various industries are utilised, such as waste from the tin-box makers, tinned iron cuttings, waste from wire-drawing, contractors' works, and old iron generally, these forming a cheap and comparatively economical raw material. The acid residue from oil refineries, the tar obtained in refining petroleum, containing about 50 per cent. of sulphuric acid expressed as SO_3, and the waste liquor from sulphuric acid works, are all frequently used for this purpose.

The treatment is carried out in a copper vat, the bottom of which is supported by cast-iron plates, the vat being heated by direct fire with flues for the hot gases carried round the sides. The usual shape is rectangular with rounded corners. The gases and vapours liberated during the operation are carried off through a chimney stack. The vat being charged with sulphuric acid, and diluted if necessary, is heated to boiling, and the scrap-iron is thrown in, the mass being stirred as frequently as possible. When the reaction is finished the charge is drawn, left to settle, and the clear liquor removed for crystallising.

According to W. P. Thompson, the residual tar from petroleum refining can be profitably utilised for the production of ferrous sulphate on the one hand, and, on the other, of a kind of bitumen suitable for various purposes. The process in question has been described by Rave. The acid tar, which may amount to about 25 per cent. by weight of the refined petroleum, is mixed with sufficient iron turnings to completely neutralise the acid. The reaction is complete after a certain time, and the mass is treated with boiling water to separate the tar from the ferrous sulphate. The tar resembles bitumen in appearance and properties, and can be thickened by heating in a still.

101. **The Buisine Method.**—This method is based on the same principle as that of Spence, from which it differs, however, in the mode of application.

In principle the Buisine method consists in treating imperfectly roasted pyrites with hot concentrated sulphuric acid. The object of this imperfect roasting is to bring the disulphide of iron into a condition less rich in sulphur and more readily attackable by sulphuric acid.

The disulphide itself is not attacked by this acid except at a temperature of about 250°, and furnishes ferrous sulphate and sulphur dioxide; whereas the lower sulphides are attacked at a temperature of about 100° to 110°, or below that at which sulphuric acid reacts upon sulphur to form sulphur dioxide.

The imperfectly roasted pyrites is a mixture of Fe_2O_3, the sulphides FeS, Fe_2S_3, Fe_3S_4, with a little unoxidised pyrites, FeS_2.

When this mixture is treated with hot concentrated sulphuric acid, the ferric oxide yields ferric sulphate, and the sulphides furnish ferrous sulphate, sulphuretted hydrogen, and sulphur, according to the following equations:—

$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O,$$
$$Fe_2S_3 + 2H_2SO_4 = 2FeSO_4 + 2H_2S + S,$$
$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

The sulphuretted hydrogen, however, reacts on the ferric sulphate, forming sulphur and ferrous sulphate,

$$Fe_2(SO_4)_3 + H_2S = 2FeSO_4 + S + H_2SO_4;$$

and if there is any excess of sulphuretted hydrogen, this is decomposed by the hot concentrated acid,

$$3H_2S + H_2SO_4 = 4S + 4H_2O,$$

so that finally the products consist entirely of sulphur and ferrous sulphate.

The whole of the sulphur originally contained in the imperfectly roasted pyrites is left in a free state. If the pyrites contained at least 10 per cent. of sulphur the quantity of sulphuretted hydrogen formed is sufficient to reduce the whole of the ferric sulphate formed at the same time; but when the roasted pyrites contained less than 10 per cent. of sulphur the mixture consists of ferrous sulphate and ferric sulphate, the proportion of the former being in direct ratio to the amount of sulphur in the pyrites. Consequently it follows that, to obtain sulphur and ferrous sulphate exclusively, it is preferable to work with imperfectly roasted pyrites containing at least 10 per cent. of sulphur.

As regards the pyrites, *i.e.* the iron disulphide left unoxidised in the imperfectly roasted mass, it does not react upon sulphuric acid under the conditions prevailing, and is consequently found in its entirety in the residue and returned to the furnace. In fact, the disulphide is not attacked by sulphuric acid below about 250°, whilst, as we shall see later, the actual temperature attained is not over 180°.

The method of working is very simple, and does not require any special plant beyond that in general use in chemical works.

In the first stage the pyrites is imperfectly roasted in ordinary furnaces (*e.g.* those of Malétra), the sulphur dioxide formed being conveyed to the leaden chamber; the crude pyrites, which contains 50° to 52° of sulphur, is thus modified, so that the sulphur content is between about 10 and 35 per cent. Next, the roasted pyrites is agitated with 60° Bé. sulphuric acid in about the following proportions: 100 to 125 parts by weight of sulphuric acid to each 100 parts of roasted pyrites. The apparatus consists of a cast-iron retort, covered in such a manner as to afford connection with a washer (*e.g.* a coke tower), and is heated by a fire underneath. As the temperature approaches 100° the reaction becomes fairly energetic, and the temperature rises to between 150° and 180°, at which point it is maintained for about a quarter of an hour. During this reaction steam is given off, and carries away with it a little sulphur, as well as traces of sulphur dioxide and sulphuretted hydrogen, which are retained by the washer. The crude product is then treated with hot water, the resulting solution depositing crystals of ferrous sulphate when cooled.

The insoluble residue contains, in a free state, almost the total amount of sulphur present in the roasted pyrites, which sulphur can be separated either by fusion, distillation, or extraction with carbon disulphide.

In this manner the whole of the iron in the pyrites can be converted into ferrous sulphate, and theoretically about 50 per cent. of the original sulphur can be extracted, the remainder being consumed in the production of the sulphuric acid taking part in the reaction. The sulphur thus obtained in considerable proportion, as a residue of the ferrous sulphate process, correspondingly reduces the cost of the product, which is thus brought down to a minimum.

It will be understood that the imperfect roasting of the pyrites may, in certain cases, be advantageously replaced by distillation in a closed vessel as already indicated, which furnishes the same result and facilitates the recovery, by condensation, of that portion of the sulphur which has to be removed from the pyrites to enable the reaction to take place.

If the pyrites employed be of a cupreous character the method just described furnishes, as crude product, a mixture of sulphur, ferrous sulphate, and copper sulphate, the proportion of sulphur being greater or smaller according to the amount present in the roasted pyrites. This mixture may be used direct for agricultural purposes, particularly for treating certain diseases of the vine; and, in fact, is largely so used, either alone or as a constituent of special mixtures. It is also clear that, if necessary, the sulphur, copper, and ferrous sulphate could be readily isolated from the crude product. This is an interesting application of iron pyrites, the considerable importance of which in chemical industries is already known.

§ 2. CONJOINT MANUFACTURE OF FERROUS SULPHATE AND ALUM

A.—Treatment of Shales

102. **Introduction.**—The pyritic shales employed for the manufacture of alum consist mainly of clay and quartz, with a variable proportion of felspar, in a more or less advanced stage of decomposition; in addition to this substance, pyrites, potash, lime, magnesia, and carbonaceous matters are also present. The colour is generally dark, blackish or brownish, occasionally bluish. These shales are chiefly found in Sweden, Norway, and Belgium, at La Tarentaise, Whitby, Glasgow, and also at Lautenthal in the Harz Mountains, and in several parts of Thuringia, Westphalia, etc. The deposits are mainly situated between the oldest sandstone and the orthoceratic chalk of the silurian age, or in the carboniferous system (Knapp). These shales are of somewhat variable composition, as will be evident from the subjoined analytical tables furnished by Knapp.

As a rule, apart from iron sulphide, the matter soluble in acids represents a very small fraction of the total substance. When freshly extracted, the proportion soluble in water is extremely low, and contains no salt of aluminium or iron.

When exposed to the air, these shales, especially when rich in iron sulphide, effloresce and crumble down. This phenomenon, which, moreover, forms the basis of the treatment to which they are subjected, is due to the presence of pyrites, which absorbs oxygen from the air, is converted into iron sulphate, and yields sulphuric acid, which, reacting on the clay present, furnishes aluminium sulphate.

Constituents.	Shale from		Constituents.	Shale from	
	Garnsdorf.	Wetzelstein.		Garnsdorf.	Wetzelstein.
Iron sulphide	7·53	10·17	Silica	50·07	52·20
Silica	0·06	0·10	Alumina	8·90	17·90
Ferric oxide	0·97	2·47	Ferric oxide	1·30	3·37
Alumina	1·83	3·17	Magnesia	1·00	1·13
Lime	0·40	1·00	Lime	traces	traces
Magnesia	traces	1·02	Carbon	22·83	0·80
Soluble in acids	10·79	17·93	Insoluble in acids	84·10	75·40

Constituents.	Whitby Shale.	
	Upper Beds.	Lower Beds.
Iron sulphide	4·20	8·50
Silica	52·25	51·15
Ferrous oxide	8·49	6·11
Alumina	18·75	18·30
Lime	1·25	2·15
Magnesia	0·91	0·90
Sulphuric acid	1·37	2·50
Potash	0·13	traces
Soda	0·20	
Carbon	2·68	2·00
Moisture	traces	traces
Manganese and chlorine	4·80	0·09
Loss	...	...

Constituents.	Hurlet Shale.	Campsie Shales.		
		Upper.		Lower.
Iron sulphide	11·13	40·52 †	38·48 §	9·63
Alumina	26·96	11·35	11·64	18·91
Silica	48·28	15·40	15·40	...
Ferrous oxide	3·72	...	...	...
Lime	2·38	1·40	2·22	...
Magnesia	traces	0·50	0·32	...
Potash	0·24	0·90	...	...
Organic matter	7·69 *	29·93 ‡	31·93 ‖	...
Total	100·40	100·00	99·99	...

* And moisture.

† S=22·36; Fe=18·16.

‡ Incl. loss and 0·15 Mn.

§ S=23·44; Fe=15·04.

‖ Including loss.

103. **Efflorescence (Weathering) and Roasting.** — The object of this operation is to convert the bulk of the sulphur present into salts of iron and aluminium.

In the first place, a flat surface is covered with stamped clay, over which is laid a bed of fuel, consisting of faggots or brushwood mixed with small coal, care being taken to leave channels in the mass. This done, the mineral is piled up and the fuel is lighted. When the mass is well alight, fresh quantities of shale are added until the heap is of sufficient size. The openings left for the admission of air are then closed, and the heap is covered with a layer of spent mineral from the extractors. The object of the operation is to retard the decomposition of the mass, regulate the oxidation, and prevent the loss of sulphur dioxide and sulphur trioxide, which have a tendency to escape. By repeatedly pumping water over the surface, the temperature is maintained at a degree suitable for rendering the decomposition as complete as possible. When the oxidation is complete, and the heap has been left for a considerable time, the mineral is ready for extraction. It contains a large quantity of soluble matter, chiefly consisting of sulphates of iron and aluminium sulphate.

The following analysis (Knapp) shows the composition of oxidised Hurlet and Campsie shales:—

Constituents.	Insoluble portion.	Constituents.	Soluble portion.
Silica	36·79	Sulphuric acid . . .	8·87
Alumina	14·34	Alumina	2·08
Ferric oxide . . .	21·53	Ferric oxide . . .	1·68
Lime	2·91	Lime	1·19
Magnesia	traces	Water	10·94
	75·57		24·76

104. **Lixiviation.** — This operation is performed in large boxes with perforated bottoms, the filtering surface being composed of sleepers covered with battens, and the whole topped with a bed of brushwood. On this bottom the roasted mineral is piled to a depth of about 13 inches, and the extracting liquor is left in contact with it over night. The mother liquor from the

alum crystallising pans is employed for the first extraction, pure water being used afterwards.

The crude extracts are stored in cisterns, and after the bulk of the impurities have settled down are removed for concentration.

105. **Treating the Extract Liquor.**—The method adopted varies according to the kind of shale employed. In the case of Whitby shales, which contain a considerable amount of magnesia, the liquor contains magnesium sulphate, and the treatment pursued is to evaporate the solution to sp. gr. 1·125–1·137 in leaden vessels, the mass being then left to clarify; and, after a further concentration to sp. gr. 1·25, a sample is tested for the percentage of alum. When, as a result of evaporation, the liquor has attained a density of 1·4 to 1·5, according to its content of ferrous sulphate, it is treated with the necessary amount of potassium chloride (or sulphate) or ammonium sulphate, in concentrated solution, and is run into the crystallising pans, where the alum crystallises out, the crystals being purified by washing and repeated re-crystallisation. The mother liquor is concentrated by evaporation in order to obtain, in succession, crystals of magnesium sulphate and ferrous sulphate.

In the case of Hurlet shales the extract liquor is free from magnesium sulphate. The evaporation can be carried on in reverberatory furnaces heated from above, there being no production of any superficial incrustation to retard the conduction of heat. During this stage abundant deposits are formed of basic or dehydrated salts of iron, and of calcium sulphate. After concentration the liquor is employed in the production of alum.

B.—Treatment of Pyritic Lignites

106. **Introductory.** — The pyritic lignites known as alum earth (*terre d'alun*, *cendres de Picardie*, *cendres pyriteuses*) have been, and still are, largely employed for the manufacture of alum and ferrous sulphate. In France they have been utilised ever since the eighteenth century, and, thanks to the abundance of the mineral and the regular bedding of the deposits, they are still worked—mainly in the departments of Aisne and Oise. At one

time they constituted an important article of commerce as a stimulating fertiliser for agricultural purposes, there being in 1825 no less than fifty works engaged in the department of Aisne alone in extracting and oxidising these lignites with a view to their employment in this direction. The price of the finished product was at that time 50 centimes per hectolitre (= 1¾d. per bushel) *ex* works.

Concurrently and in the same district there were seven factories dealing with pyritic lignites, five of them producing alum and ferrous sulphate, the remaining two merely evaporating the extract liquor in order to prepare the magmas employed as raw material in the other works. With the exception of two which still survive, all these factories, and others succeeding them, have now disappeared.

The oldest of these factories is that at Urcel,* which is still in existence. It was erected in 1786 by an Englishman named Chamberlain, in virtue of a decree of the Royal State Council dated 20th May of the above-named year, by which permission was granted to the said Chamberlain, for the space of twenty years, to manufacture copperas, or *vitriol martial*, by a secret process of his own.

In 1791 the concessionnaire ceded his rights and factory to the brothers Moreau d'Olibon. For nearly 20 years the factory produced an impure green copperas, which was unable to compete with the "de Beauvais" and "English" copperas, without the nature of the impurity being known. When, however, it was recognised as alumina, or rather aluminium sulphate, and Vauquelin's labours were made known, the production of alum was carried on as well—an example followed in the other factories established at that period. Finally, in 1807, the expiring concession was renewed, in perpetuity, by the Government.

Other factories were very soon started in the same department, the second — authorised by a Governmental decree of May 5, 1802—being erected round the old Abbey of Cuissy near Beaurieux. The discovery of the vast deposit of pyritic lignite

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* Urcel is a small place in the department of Aisne, about 10 kilometres from Laon on the high road to Paris.

underlying the valley of the Aisne was made as a result of the work carried on by a Mons. de Belly de Bussy, in prospecting for coal.

In consequence of difficulties experienced in the extraction of the mineral, the Cuissy works were transferred in 1822 to the village of Bourg, about 5 kilometres away. This latter factory, which in its time attained a certain importance, has now passed away.

Following the Bourg works came those at Chailvet,* still in existence. They were installed and authorised—by a decree dated May 11, 1807—for the manufacture of copperas, alum, artificial soda (*soude factice*), and Prussian blue. The reason these works were established for the production of artificial soda was that, on account of the Continental blockade and perpetual state of war at that period between France and her neighbours, commercial relations were interrupted and no Spanish soda could be imported. However, this branch was discontinued after the peace of 1814, and Prussian blue was never at any time manufactured in a continuous manner; consequently, only alum and ferrous sulphate were produced.

The works at Quessy, about 5 kilometres from La Fère and 1 kilometre from St. Quentin Canal, were built in 1810, and authorised by a royal ordinance dated March 16, 1819. Here also the manufacture of artificial soda was carried on at first. At about the same period, namely in 1812, another factory, since disappeared, was started at Andelain.

The treatment of lignites, as carried on in the department of Aisne, was also pursued in other districts possessing analogous deposits; but, with the exception of the two factories mentioned above, all the works have now ceased operations.

The technical history of this industry in France is of only minor interest, there being scarcely any improvements to chronicle. One point, however, is interesting to record, namely, that in place of the peat or lignite at first employed as fuel in nearly all the works, coal is now used. In other respects little or no changes

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* Chailvet is a small place about 1 kilometre north of Urcel and some 10 kilometres away from Laon.

have been made, and the sum-total of the advance made is, so to speak, *nil.*

This is due to the long-continued era of prosperity enjoyed by the manufacturers, owing to the absence of any competition which, by lowering prices, would have obliged the producers of alum and ferrous sulphate to work more economically. Another reason was the lack of technical education amongst them, in consequence of which periods of crisis found them unarmed; and, in addition, the absence of unity between the manufacturers of aluminous products led them into internecine struggles instead of endeavouring to combine against foreign competition.

Matters began to draw to a head after 1866, owing to the development of the new aluminium sulphate industry founded in France by Messrs. Pommier of Gennevilliers. Very shortly after, this competition was intensified by the expansion of the alum industry in other countries, and the importation, at low prices, of English alum (mainly Spence's), Belgium alum and aluminium sulphate from the Ampsine factory, Italian alum from La Tolfa, etc., the last named afterwards becoming established at Rouen, where a factory for treating La Tolfa alunite was built under the very windows of the Malétra works.

The Aisne alum manufacturers, who were at the head of the market, believed their trade was ruined, whereas it was only compromised; and, wishing to make the most of their factories while there was still time, they raised their prices. The logical consequence of this step was to hasten the displacement of alum by aluminium sulphate, which at first had made small headway owing to defects in manufacture and conservatism on the part of various consumers.

Finally, the result was a general break-up in the price of alum, and a diminution in the demand. The struggle, however, adjusted itself, and a syndicate combined a number of French producers. For the Aisne alum makers this was merely a palliative, not a cure, but fortunately they had ferrous sulphate to fall back upon, and, though the demand was at first small, the trade grew, prices kept up, and for some years makers were able to work at a profit.

This state of things was, however, transitory, and not even the continually increasing call for ferrous sulphate, its ready sale, and, of late, the imposition of a protective duty on alum, could arrest the decadence of the industry employing lignites. Purer and drier grades of ferrous sulphate than those produced by the alum makers were put on the market by English competitors, and in consequence of the utilisation of previously wasted ferruginous bye-products from other industries—metallurgical and oil refining—the resulting fall in prices hastened the fall of most of the lignite treaters in France. At the present time only two important factories of this class have been able to survive, as a result of a combination of economic considerations, such as position, proximity to means of communication, and powerful equipment. These two works, one at Chailvet, the other at Urcel—two adjoining communities in the department of Aisne—still turn out about 2500 to 3000 tons of alum—about $\frac{1}{4}$ of the total consumption—every year, and 5000 to 6000 tons of ferrous sulphate.

107. **The Raw Material.**—*A*. DEPOSITS.—Pyritic lignites are extremely abundant in certain localities. They are of very frequent occurrence in the extensive plains of Northern Germany, deposits being found near the Oder, at Freinwald, Gleissen, Schermeisel, and Muskau; others at Mansfeld, Bornstedt, Holdenstedt, and finally at Schwemsal on the Mulde.

In France several deposits occur in the department of the Rhone, and others in Picardy, Oise, the Ardennes, Champagne, etc., the largest, most regular, and most easily worked, however, being those in Aisne.

The deposits were formed in stagnant lagoons during the Tertiary period. An examination of the geology of Aisne shows that the cretaceous formations, which occupy a large area in Thierache, the Picard and Champenois districts, disappear towards the south-west under the tertiary plateaux of the Laon district, extending from Laon to the southern border of the department. They are arranged in parallel planes sloping from N.E. to S.W., so that the formations appearing on the surface of the northern plateaux are found to occupy progressively lower positions on the slopes of the intersecting valleys farther south, and finally, in the southernmost valleys, form the beds of the valleys themselves. The arrangement of the entire series of tertiary beds is in the following order:—Plastic clays underneath, resting on white chalk; then, in succession, nummulitic sands, coarse lower and upper limestones, Beauchamp sands and sandstones, St. Ouen travertine, gypsum, green marls and pottery clay, Brie travertine, Beauce travertine, Fontainebleau sands, and millstone clays.

The plastic clay found on the surface in the Vermandois district, the mass of which is of cretaceous origin, forms the base of the Laonnois plateaux. It also at one time covered the Souche district, where it has left as evidence a number of isolated hills covered with thick beds of diluvial sand. Even at one end of the Laonnois district it is superposed on a thick bed of Bracheux sand,—the remains of the newest cretaceous beds, which have entirely disappeared from the Souche basin, and are masked by plastic clay in the Vermandois district, but reappear in the high Thon valley.

At the base of the plastic clay are lacustrine marls and limestones, worked, for the production of hydraulic lime, in the south of the department. The clay itself encloses the pyritic lignite deposits, worked for the manufacture of alum and extending for a length of 45 miles between Catelet and Reims, the breadth between Houblières and Goulancourt being 17 to 18 miles.

This clay occupies the bed of the Aisne, Vesle, and Lette valleys; it is impermeable, and forms the main water-level of the department.

The section of the strata at Chailvet, Urcel, etc. (Fig. 113), shows, in the first place, immediately below the surface mould, a bed of siliceous sand, enclosing in places reniform masses of soft sandstone, which here and there is replaced by a workable (and actually worked) layer of hard sandstone. This sandstone is rich in *flora*, leaf prints of laurel, oak, chestnut, sallow, etc. being very plentiful. The animal kingdom is represented by shells, mainly cerites, embedded in siliceous cement.

Underneath this layer is an interesting shell-gravel of considerable thickness, constituted by the agglomeration of an infinity of various shells—*cerithium*, *melania*, and, above all, *ostrea belloracina*, many of which are in a perfect state of preservation. This gravel is used for ballast; but, despite its high percentage of calcium carbonate and its approximation to the composition of hydraulic limestones, the attempts made to work it up for lime have proved failures.

Next follows a very compact layer of sand, agglomerated by an argillaceous cement; and we then come to a workable deposit, 6 to 10 feet thick, composed of alternate strata of pyritic lignite and aluminous clay resting on a bed of clay 10 to 13 feet thick. The top part of this clay bank is black, laden with organic matter, and rich in pyrites; the lower portion white. The content of alumina varies between 20 and 28 per cent., and it is worked for brick-making.

Between the clay bed and the seam of lignite is a stratum enclosing a large number of renal concretions of pyrites, all scattered on the same horizontal level.

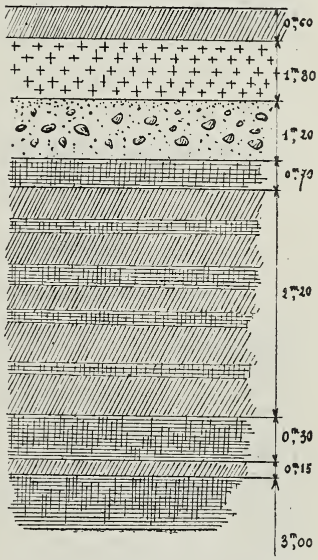


FIG. 113.—Section of the strata at Chailvet (Aisne).

The deposits, however, are not all of uniform regularity, the bed being at Chermizy, for example, much thicker, more clayey, and containing veins of dolomite.

B. COMPOSITION AND PROPERTIES OF THE ORE.—The composition of these ores varies considerably with the locality and the place where the samples are taken. At Chailvet the top layers are very poor in pyrites (8 to 9 per cent.), that in the middle of the bed is a little richer (12 to 15 per cent.), and the lower portion is very rich indeed (20 to 30 per cent.). The following table shows the limits of variation.

The percentage of organic matter is from 20 to 30 per cent. From the manufacturing point of view, an average of 15 per cent.

of iron disulphide can be counted upon. In addition to this principal element, the pyritic lignites contain a notable quantity of clay, a high proportion of ferric oxide combined with the organic matter, a little magnesia and chalk, traces of phosphoric acid and potash, and 0·2 to 0·3 per cent. of nitrogen.

Constituents.	1	2	3
Water	34·80	22·60	40·00
Iron pyrites	23·70	30·40	9·50
Sulphuric acid	nil	trace	trace
Residue non-volatile at red heat	27·00	39·00	34·60

At Bornstedt three classes of ore are found, the analyses of which are given below (Knapp):—

Constituents.	Alum Mineral.	Alum and Vitriol Mineral.	Vitriol Mineral.
Silica	33·34	14·02	11·51
Sulphuric acid	0·27	0·67	0·77
Chlorine	...	0·10	0·15
Alumina	18·73	9·65	5·24
Lime	1·16	0·73	1·75
Magnesia	1·08	1·02	0·92
Soda	0·19	1·14	1·00
Potash	1·78		
Ferrous oxide	2·53	5·22	6·88
Iron disulphide	2·75	19·27	20·38
Sulphur	2·65	1·87	3·32
Organic matter and moisture	34·63	45·64	46·93
Total	99·11	99·33	98·85

The colour of the pyritic lignites varies from greenish black to lustrous black. They are more or less compact. In the fresh condition they yield up no sulphates to water, with the exception of a minute quantity of calcium sulphate. They exhibit the same property as the pyritic shales of weathering on exposure to air, heat being liberated and soluble salts formed.

They are always more or less mixed with sand and clay, and sometimes contain flakes of mica. Neither sulphur nor pyrites can be detected by the unaided eye or under the magnifying glass. Nevertheless, by means of careful levigation, a small quantity of pyritic granules can be obtained from the clay separating the strata of lignite. A small quantity of free sulphur and resinous bodies can be extracted by means of carbon disulphide.

Boiling hydrochloric acid attacks pyritic lignite, furnishing a greenish-yellow liquid, and liberating a very small quantity of H_2S. The liquid chiefly contains ferrous chloride, with traces of ferric chloride. When strongly heated the pyritic lignite parts with sulphur, which sublimes. This property is due to the presence of pyrites.

C. METHOD OF WORKING THE DEPOSITS.—The first thing is to remove the top soil in trucks. The workmen, under the supervision of a foreman, who has also to keep the tramways in order, get out the soil with picks and dump it in the hollows left by previous extractions. The lands thus reconstituted are sterile and cannot be replanted for 4 to 5 years. Each truck is served by three men, who receive on an average 3 francs per diem; and the amount of earth removed is about 8 or 9 cubic metres (12 to 13 cubic yards) per man (computed on the space actually cleared), the work thus costing about 35 centimes per cubic metre ($2\frac{3}{4}$d. per cubic yard).

This preparatory work is carried on during the winter, and the actual winning of the mineral is commenced in the month of April. The lignite is taken out in steps, and, by reason of the compact nature of the mineral, costs 40 centimes per cubic metre (3d. per cubic yard). The seam being immediately overlying a bed of clay, the work is often retarded by water, which has to be drained off through channels cut for that purpose through the workings.

The mineral is conveyed to the works in trains of 5 or 6 trucks, and is there tipped in long, parallel, prismatic heaps, measuring about 3 cubic metres per running metre, as shown in section in Fig. 114. Since each of the existing works in France deals with 10,000 to 14,000 cubic metres of mineral per annum, it is evident that the superficial area required is considerable.

Occasionally, when the labour of open cast working is too difficult and expensive, the mineral is got by driving headings. This system, however, has little to recommend it, since a considerable quantity of mineral has to be left in the form of pillars to support the roof; and inconvenience is often caused by water.

D. PREPARATION OF THE MINERAL.—The preparation of pyritic lignites, in view of their ulterior treatment for alum and ferrous sulphate, is very similar to that pursued with shale. The nature of the various constituents renders them particularly susceptible to oxidation; and in fact, under the influence of aëration and moisture, pyrites is not slow to fix oxygen. The temperature in the interior of the heaps rises rapidly, and if the operation is allowed to continue for a month or six weeks the mineral takes fire spontaneously. This, however, is not waited for, the oxidation being assisted and regulated by turning the heaps over with shovels to facilitate the access of air, whilst, at the same time, small fires (Fig. 115) are kindled at intervals and covered up as required. To enable the combustion to extend, three flues are constructed of faggots.

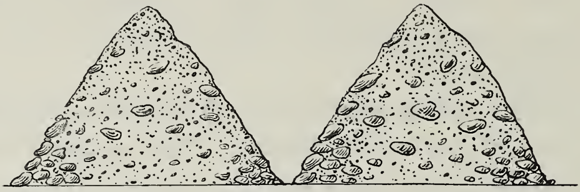


FIG. 114.—Preparing the mineral.

The work of this first stage—*retenage*, as it is called—costs about 10 or 12 centimes per cubic metre ($\frac{3}{4}$d.–1d. per cubic yard).

Under the influence of this treatment, and provided the climatic conditions are favourable, oxidation proceeds actively, and combustion slowly progresses from the centre of the heaps outwards, a whitish or yellowish efflorescence forming on the surface, and an abundance of steam, carbon dioxide, and sulphur dioxide being disengaged. When the fire reaches the surface, and combustion becomes too energetic, the temperature of the ignited mineral is moderated by covering the heaps with wet spent mineral from the extractors,

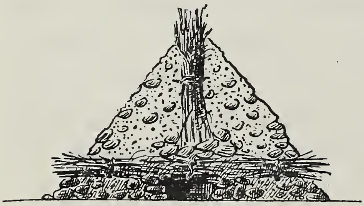


FIG. 115.—Firing the heap.

and pumping water into the mass. At the end of 3 or 4 weeks the mineral is ready for the second stage, the object of which is to extinguish the fire (whilst still aërating the mass) and prevent the total destruction of the ferrous sulphate under the influence of a progressively heightened temperature. After leaving the mass to ripen for some time, it is put in larger heaps before the bad weather comes on. These heaps measure 20 metres across the base and 12 metres high, and their size is sufficient to protect them against the rains. The mineral is then ready for lixiviation, but may with advantage be left to age a little longer, this considerably improving the quality as a result of complementary oxidation and various secondary reactions. The loss in weight during combustion is about $\frac{1}{4}$th to $\frac{1}{3}$rd.

The reactions occurring throughout this prolonged period and the successive manipulations are of the following nature:—The efflorescence is due to the fixation of atmospheric air by the pyrites, and the production of ferrous sulphate and sulphuric acid, the latter then acting on the alumina of the clay to form aluminium sulphate, according to the following simple reactions:—

$$(1)\quad FeS_2 + 7O + 8H_2O = FeSO_4, 7H_2O + H_2SO_4,$$

$$(2)\quad 3H_2SO_4 + Al_2O_3 = Al_2(SO_4)_3 + 3H_2O,$$

though in reality matters do not proceed in such a simple manner.

At first a portion of the sulphur distils and forms magnificent lemon-yellow crystals on the surface of the heap. On the other hand, the conversion of the pyrites into ferrous sulphate, with the production of sulphuric acid and subsequent formation of aluminium sulphate, is far from being so simple as the above equations would imply. The amount of sulphuric acid produced represents only a very small fraction of the sulphur in the pyrites, the greater part being converted into SO_2—

$$FeS_2 + 6O + 7H_2O = FeSO_4, 7H_2O + SO_2.$$

A fractional portion of the SO_2 is lost by dissipation into the air, along with the water vapour and carbon dioxide resulting from the combustion of the organic matter. The rest is retained in the heap, and, in the presence of water vapour and the porous cinder, absorbs oxygen, thus forming sulphuric acid, which acts on the alumina of the clay. This reaction is greatly assisted by the presence of water vapour, and it is for this reason that the occurrence of spontaneous ignition is not awaited, since not only would that proceed from the surface towards the centre, which would be unfavourable to the utilisation of the sulphur, but also would go on in a desiccated medium and produce nothing but a large quantity of ferric oxide or insoluble sub-salts, and a relatively small amount of aluminium sulphate. Consequently the roasting fires are lighted whilst the material is still damp.

Ferrous sulphate is unstable; it absorbs oxygen, and is converted into soluble ferric sulphate and insoluble sub-salts. At the time of roasting, the heat is sufficiently intense to decompose a portion of these iron salts; and ferric oxide is formed simultaneously with the liberation (distillation) of sulphuric acid, which attacks the clay immediately. This decomposition of the iron salts would be carried almost to completion were it not interrupted by the second handling; and, in fact, the old alum makers followed this course, the red cinder obtained by them being very rich in aluminium sulphate but poor in ferric sulphate, and particularly so in ferrous sulphate.

Both ferric oxide and ferric sulphate play a part in the production of aluminium sulphate, their oxidising properties enabling them to convey oxygen to sulphurous acid and convert it into sulphuric acid. Moreover, the mineral, when lixiviated immediately after roasting, yields a lower proportion of aluminium sulphate than when it has been left to mature a long time in large heaps. Here not only the extra oxidation, but also the reaction of the oxidation products on the excess of clay in the material, have to be taken into account, since both ferrous and ferric sulphate in time react on alumina and form the sulphate of that base. As this action, though gradual, certainly exists, it becomes a matter of interest to watch over the cinder previous to lixiviation.

The reactions going on in the heap are therefore of an extremely complex nature. They are in all respects identical with those occurring in the treatment of shales, and are very difficult to regulate, atmospheric conditions—which vary from year to year—being a factor of the highest importance.

The composition of the material ripe for lixiviation may therefore be expected to vary within very wide limits; and that this is actually the case the following analyses will show:—

Constituents.	1	2	3	4	5	6	7	8	9	10	11	12
Water	19·60	16·80	15·50	..	..	16·40	15·70	..	..	10·80	13·80	..
Ferrous sulphate ($FeSO_4$, $7H_2O$) .	3·55	6·07	11·50	13·70	6·30	5·60	9·40	9·80	13·30	10·27	12·41	16·41
Ferric sulphate ($Fe_2(SO_4)_3$, $9H_2O$)	6·92	4·74	2·00	1·50	4·90	4·90	1·50	2·40	0·80	2·30	0·75	5·52
Aluminium sulphate ($Al_2(SO_4)_3$, $16H_2O$)	7·34	13·20	9·80	9·10	3·30	6·00	6·00	6·90	7·80	5·26	3·01	8·02
Calcium sulphate ($CaSO_4$)	1·50	..	0·73	..	..	..	..	..	..	..	..	..
Sulphur trioxide (SO_3)	..	11·60	8·08	..	..	..	..	..	..	12·80	10·80	11·30
Insoluble in water .	59·60	58·00	66·00	..	..	..	..	..	..	70·00	68·00	67·80

The insoluble matter consists chiefly of organic substances, silica, unattacked clay, iron peroxide, a little of the soluble sulphates, unoxidised sulphur, etc.

The cost of the mineral when ready for lixiviation varies according to the year, but may be estimated on the following basis, in shillings per cubic yard (about 15 cwt.):—

Extraction, Haulage, etc.	Cost of Tools.	Turning.	Piling in heaps.	Rent of Ground.	Interest, Depreciation, etc.	Total Cost per cubic yard.
1·212	0·091	0·182	0·182	0·121	0·333	2·121

108. **Manufacture of Ferrous Sulphate.**—This entails the handling of a very considerable volume of liquor, and consequently, to keep the expenses within reasonable bounds, the works are generally laid out on a slope to enable the liquid to flow by gravitation from one department to another, the lixiviation plant being situated on the highest level. A plan of the general arrangement of works for treating pyritic lignites is shown in Fig. 116.

A. LIXIVIATION.—This operation is intended to separate the soluble matters in the oxidised mineral from the insoluble portion. The plant comprises—

(1) A series of dressed stone tanks G, G, G (Fig. 118), lined with a false bottom of boards supported on beams H, H, and carrying a thick filtering layer of brushwood I, I. Each tank is connected with its neighbour by a conduit K, arranged in such a

manner that the liquor drawn off from No. 1 (for example), at the bottom, is discharged into the top of No. 2. Moreover, each tank can be put in communication with any other member of the series by means of a system of conduits L, L, which also serves to

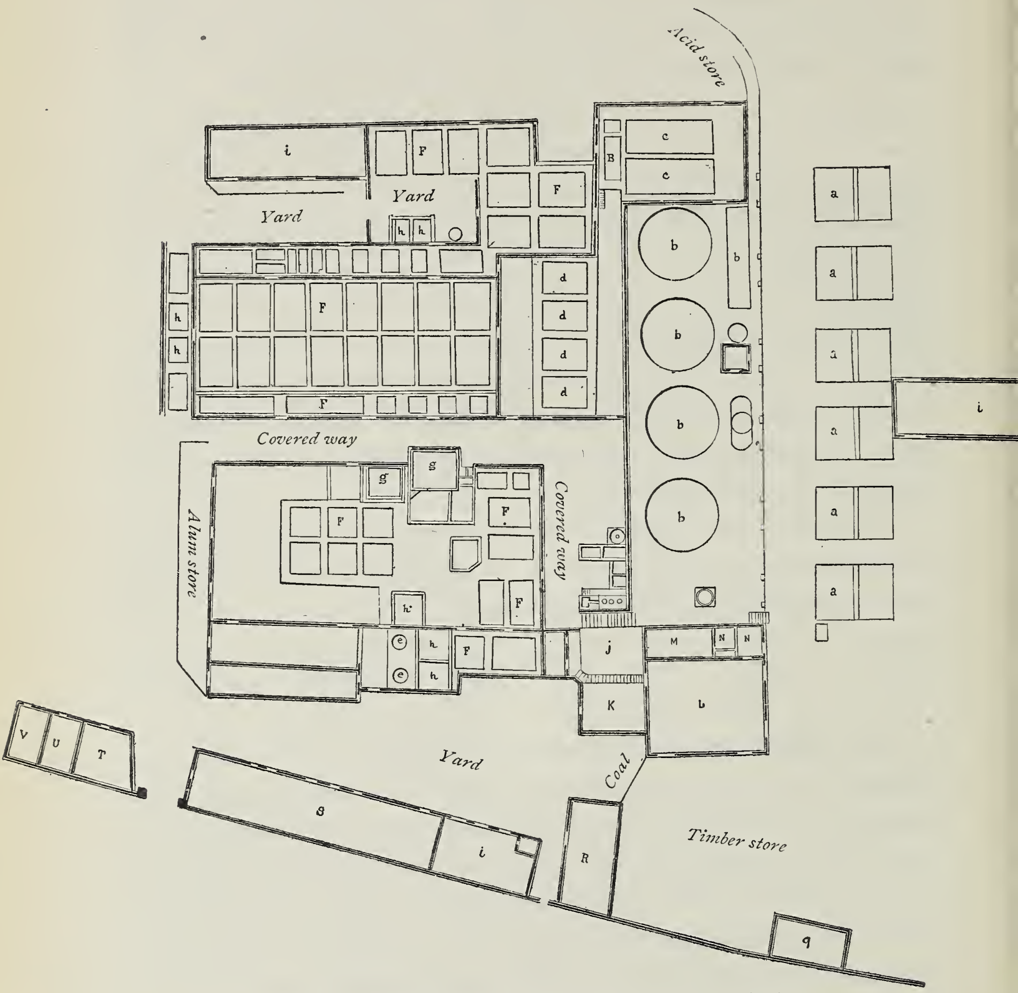


Fig. 116.—General plan of works for treating pyritic lignite.

a, Lixiviation tanks; *b*, receptacles; *c*, preparatory tanks; *d*, lead-lined tanks; *e*, copper tanks; F, crystallisers; *g*, leaden re-casting boxes; *h*, leaden turbines; *i*, stores; *j*, generators; K, engine; L, sawmill; M, laboratory; N, offices; P, dwelling-house; Q, fire engine; R, soldering shed; S, dwellings and offices (accommodation for 4 foremen); T, carman's rooms; U, forge; V, cart house. Part of the stores, cooperage, stables, forage shed, granary, mechanics' and plumber's rooms, iron stores, water reservoirs, etc., are situated outside the limits of the plan.

convey the weak liquor employed for lixiviation. Fresh water is supplied, through a conduit M, to each tank.

In front of each of the tanks is a small reservoir N, N, into which the liquor drains through the opening P after traversing the layer of mineral O. This reservoir communicates with the exterior by two conduits, one of which, Q, discharges the strong liquor into a channel R, which delivers into the temporary storage reservoir S, whilst the other T serves to drain off the weak liquor, which runs away through the channel U into the cistern V.

The system of canalisation is formed of leaden pipes, or else of hollowed tree trunks embedded in masonry, the circulation of the liquor being regulated by wooden plugs. The tanks and reservoirs are of dressed stone, and, to prevent leakage, are surrounded by jackets of clay followed by a layer of rammed chalk.

(2) A pump, or Körting injector, raises the weak liquor from the cistern V, and returns it to the lixiviation tanks.

(3) A set of tracks and points for the tramway trucks.

The lixiviation is carried on in the open air and in a systematic manner. At Chailvet the installation is composed of eight "elements," of about 1080 square feet in superficial area and 3 feet in depth, forming two separate batteries.

Each "element" takes a charge of about 3 tons, spread out to a depth of some 16 inches. It is delivered in trucks, and each workman, in return for a daily wage equivalent to 3 shillings, has to bring 12 cwt. of mineral to the lixiviation tanks, spread it, and afterwards remove the corresponding quantity of residue to the waste heap.

In a normal season the strong liquor measures 28° of the Baumé hydrometer, the weak liquor having a density of 10° Bé. A cubic yard of cinder will yield about 99 gallons of 28° Bé. liquor. The quantity obtained, however, varies between somewhat wide limits, according to circumstances, such as the richness of the mineral, the percentage of moisture, etc.; and the same also applies to the density. Nevertheless, it is but seldom that the figures fall below those cited.

The 28° Bé. liquors collected in the reservoir S deposit there the clay and impurities with which they are laden. They then have a dark reddish-brown appearance, and contain all the soluble constituents of the cinder, but vary considerably in relative composition, according to the nature of the cinder under treatment, as the following figures will show :—

Composition in Grams per Litre

Constituents.	1	2	3	4	5	6	7
Aluminium sulphate ($Al_2(SO_4)_3$)	94·00	136·00	...	150·00	110·00	126·00	94·00
Ferric sulphate ($Fe_2(SO_4)_3$) . .	58·00	61·00	123·00	75·00	57·00	...	46·00
Ferrous sulphate ($FeSO_4$) . . .	68·00	110·00	55·5	105·00	164·00	...	65·00
Calcium sulphate	2·5	...	111·00	...	...	0·90	...
Dry residue . .	258·00	319·00	319·00	...	...	...	...
Specific gravity .	1·215	1·263	1·263	1·290	1·213	1·274	1·230

The lixiviation residue is a source of great trouble. Attempts have been made to utilise it as fuel for evaporating the liquors, by burning it on a hearth with forced draught. However, this had to be abandoned by reason of the low percentage of carbon, in consequence of which the evaporation went on only

Figs. 117 *to* 121.—*Plan and Sections of Lixiviation Plant.*

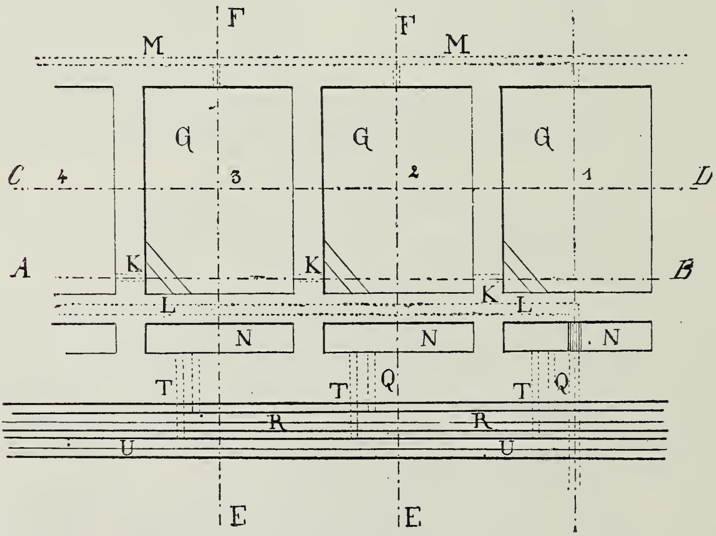
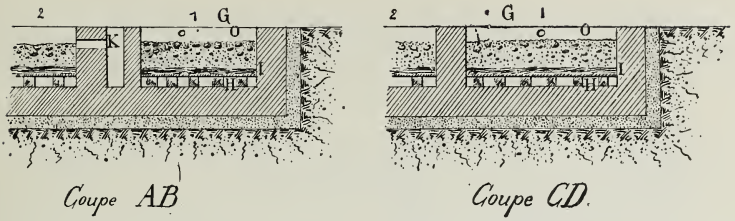


Fig. 117.—Plan.



FIGS. 118 and 119.—Transverse sections.

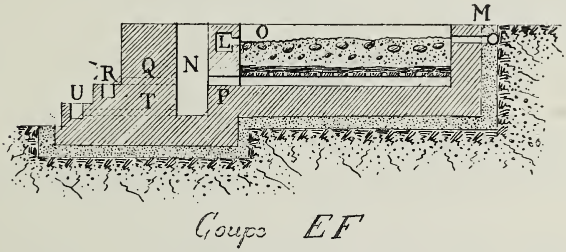


FIG. 120.—Coupe section.

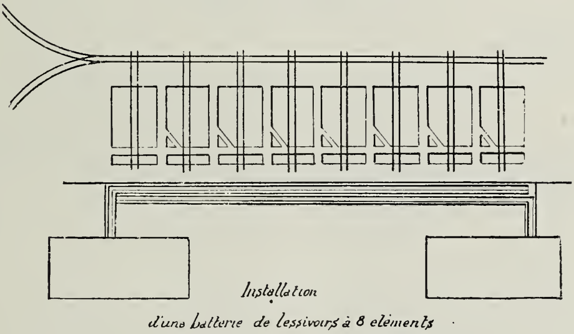


FIG. 121.—General plan, showing arrangement of lixiviation tanks, channels, reservoirs, and tramways.

very slowly, even when a large quantity of the fuel was consumed; and also on account of the extra labour involved in stoking, the vast quantity of cinders produced, and their fusible character, which led to the constant obstruction of the draught.

The analysis of this residue, by A. Vivien of St. Quentin, furnished the following figures:—

Water	25·28	Carbon	9·55
Organic matter	18·98	Volatile carbonaceous matter	9·33
Mineral matter	55·74		
	100·00		

Sulphur (as pyrites)	2·52
Free sulphur	0·17
SO_3 in combination	2·71

In order to calculate the calorific power of this residue as fuel, the composition may be conveniently expressed as follows:—

Water	25·28		
Carbon	11·63	Organic matter	18·98
Hydrogen	1·30		
Oxygen and nitrogen	6·32		
Sulphur (as pyrites)	2·52	Mineral matter	55·74
Free sulphur	0·17		
SO_3 in combination	2·71		
Metals and oxides	50·34		
	100·00		

We then have:—

(1) Heat disengaged by the combustion of the carbon—

$$11{\cdot}63 \times 8080 = 93970{\cdot}40 \text{ cal.}$$

(2) Heat disengaged by the combustion of the hydrogen, assuming the 6·32 per cent. of oxygen *plus* nitrogen contains 4·32 of oxygen—

$$29{,}000\left(1{\cdot}03 - \frac{4{\cdot}32}{8}\right) = 14{,}210 \text{ cal.}$$

(3) Heat disengaged by the combustion of the free sulphur and the sulphur in the pyrites—

$$2162 \times 2{\cdot}69 = 5815{\cdot}78 \text{ cal.}$$

Or a total of

$$93970{\cdot}40 + 14210{\cdot}00 + 5815{\cdot}78 = 113996{\cdot}18 \text{ cal.}$$

Allowance must, however, be made for loss: thus

The evaporation of the moisture present absorbs an amount of heat estimated by the formula

$$Q = P(606{\cdot}5 + 0{\cdot}305 \times t - \theta).$$

Then, assuming the evaporation to be effected at 100° C., whilst the initial temperature of the fuel is 15° C.,

$$Q = 25(606{\cdot}5 + 0{\cdot}305 \times 100^\circ - 15) = 15{,}560 \text{ cal.}$$

Or, taking the final temperature of the vapour as 300° C., the last-named value becomes

$$15{,}560 + 25 \times 200 \times 0{\cdot}475 = 17{,}935 \text{ cal.,}$$

0·475 being the specific heat of water vapour.

Again, a certain amount of heat is consumed in decomposing the pyrites; and this may be approximately estimated, the heat of formation being 750 cal. per each 1 kilo. of sulphur combining with iron. The heat absorbed in the decomposition of the pyrites will therefore be

$$750 \times 2{\cdot}52 = 1890 \text{ cal.}$$

Altogether there are 2·69 kilos. of sulphur, furnishing 5·38 kilos. of SO_2. To this must be added the sulphur in combination as sulphates, namely 1·08 kilos., yielding 2·16 kilos. of SO_2, the total SO_2 produced being therefore 7·54 kilos. This gas being liberated at 300° C. (an assumption made in order to simplify the calculation), and its specific heat being 0·409, the amount of heat lost from this cause will therefore be

$$7{\cdot}54 \times 0{\cdot}409(300 - 15) = 878{\cdot}9 \text{ cal.}$$

On the other hand, heat is absorbed in the decomposition of the SO_3, namely

$$\frac{2{\cdot}71 \times 2300}{8} = 77 \text{ cal.,}$$

2300 being the difference between the heat of formation of the sulphur combining with oxygen to form SO_3, and that of the same quantity of sulphur in forming SO_2.

The 11·63 kilos. of carbon produce 42·64 kilos. of CO_2, the specific heat of which is 0·2025. The heat consumed in this respect will be

$$42{\cdot}64 \times 0{\cdot}2025 \times 285 = 2463{\cdot}82 \text{ cal.}$$

Again, the 2 kilos. of nitrogen (in the fuel) account for a loss of

$$2 \times 0{\cdot}244 \times 285 = 139 \text{ cal.}$$

The next item to be estimated is the amount of nitrogen in the air required to support the combustion of the fuel. Taking first the theoretical quantity, we find that

Oxygen required for the combustion of	11·63 kilos.	of carbon	=31·01 kilos.
,, ,, ,,	0·49 ,,	hydrogen	= 3·92 ,,
,, ,, ,,	2·69 ,,	sulphur	= 2·69 ,,
		Total . . .	37·62 kilos.

This corresponds to 163·56 kilos. of air, of which 125·94 kilos. is nitrogen. The quantity of heat abstracted on this score is

$$125{\cdot}94 \times 0{\cdot}244 \times 285 = 8789{\cdot}40 \text{ cal.}$$

The heat removed by the water resulting from the combustion of the hydrogen is

$$9{\cdot}27 \times 0{\cdot}475 \times 285 = 1254 \text{ cal.}$$

On adding together these amounts of waste heat we obtain the total—

$$17{,}935 + 1890 + 879 + 77 + 2464 + 139 + 8789 + 1254 = 33{,}427 \text{ cal.}$$

Under the conditions assumed above, the combustion of 100 kilos. of residue would produce	113996 cal.
The losses of heat amount to	33427 ,,
Leaving a useful balance (combustion in presence of 1 vol. of air) of	80569 cal.

If, however, the combustion be effected in presence of a larger volume of air, the losses increase. Thus—the specific heat of air being 0·2377—for each extra volume (163·56 kilos.) of air, the loss will be augmented by

$$163{\cdot}56 \times 285 \times 0{\cdot}238 = 11{,}094 \text{ cal.}$$

When, as is usually the case, combustion takes place in presence of a threefold volume of air, the amount of residual available heat will therefore be only

$$80{,}569 - 11{,}094 \times 2 = 58{,}381 \text{ cal.};$$

a very low figure, although no allowance has been made for the other losses specified above.

If we desire to estimate the amount of such fuel required for the concentration of the lixiviation liquor, the calculation is now easily made.

Assume that 1 cubic metre of liquor measuring 28° Bé. has to be concentrated to 42° Bé. strength,

The specific gravity corresponding to 28° Bé. is $d = 1{\cdot}2407$,
" " " 42° Bé. is $d' = 1{\cdot}4100$.

Then, taking V to represent a certain volume of solution, of specific gravity d; and x the weight of water to be evaporated in order to bring the specific gravity up to d', we may set down the equation as

$$Vd - x = (V - x)d',$$
$$Vd - x = Vd' - xd',$$
$$V(d' - d) = x\,(d' - 1),$$

from which

$$x = V\frac{d' - d}{d' - 1}.$$

Hence, taking V = 1000 litres,

$$x = 1000 \frac{1{\cdot}4100 - 1{\cdot}2407}{1{\cdot}410 - 1} = 413 \text{ kilos. of water.}$$

If we now apply the formula

$$Q = P(606{\cdot}5 + 0{\cdot}305\, t - \theta)$$

and substitute as follows,

$$P = 413 \text{ kilos.}$$
$$t = 100^\circ \text{ C.}$$
$$\theta = 15^\circ \text{ C.}$$

we have

$$Q = 413(606{\cdot}5 + 30{\cdot}5 - 15) = 256{,}886 \text{ cal.}$$

as the quantity of heat theoretically requisite for the evaporation of our 413 kilos. of water. To this must be added the amount necessary to raise to 100° C. the residual volume of liquid, the specific heat of the liquor being assumed equal to 1—

$$587 \times 85 = 49{,}895 \text{ cal.}$$

The total amount of heat required is therefore

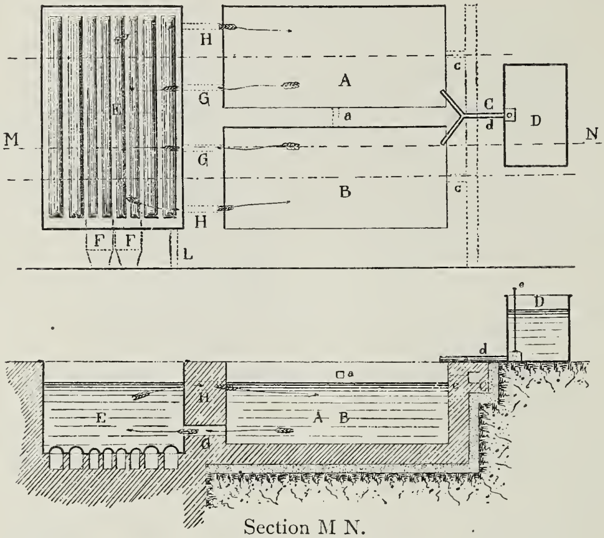
$$256{,}886 + 49{,}895 = 306{,}781 \text{ cal.};$$

a figure corresponding to a consumption of about 520 kilos. of fuel, without making any allowance for the losses. Hence this method of utilising the residue in question hardly appears practicable.

B. REDUCTION (VERDISSAGE) OF THE LIQUOR. — The presence of ferric sulphate in the liquors is objectionable, since, in the subsequent operations, it would form iron alum, and thus contaminate the potassium-, or ammonium alum, produced. It is removed by reduction, *i.e.* conversion into ferrous sulphate, under the influence of iron and sulphuric acid.

With this object, the liquor in the storage reservoir is transferred by means of a conduit C (Figs. 122 and 123) and gulleys *c* to two dressed-stone tanks A and B, connected by an aperture *a*, which is kept closed during the treatment.

At one side is a leaden boiler E, heated by two furnaces F, F, and communicating with the tanks A, B by conduits G, H. A leaden vat D containing sulphuric acid discharges into the two tanks through a branched pipe *d*, which is closed by a leaden plug *e*. On raising the latter the desired quantity of acid—15 to 20 kilos. (33 to 66 lbs.) of 60° Bé. acid per cubic metre (220 galls.) of liquor—is run into the tanks, and a certain quantity of scrap-iron is thrown in. Heat is then applied to the boiler, and, owing to the arrangement of the conduits H and G, an inverse current is set up between this vessel and the tanks, the cold liquor from the latter passing from A or B towards E, *viâ* G, whilst the hot liquor from E passes towards A or B through H. The liquor in the tanks is thus heated, and rapidly attacks the scrap-iron, itself gradually turning green, so that, at the end of about 12 hours, all traces of ferric sulphate will have disappeared and the liquor is ready for evaporation.



Section M N.

FIGS. 122 and 123.—Plan and section of the reduction plant.

A, B, Reduction tanks; E, leaden boiler, with furnaces F, F; D, sulphuric acid tank; G, G, H, H, conduits connecting the boiler and tanks; C, feed pipe for the liquor to be reduced; *c*, *c*, gulleys connecting C with the tanks; *d*, feed pipe for acid; *a*, gulley connecting tanks A, B; L, discharge pipe for reduced liquor.

The process can also be effected on concentrated very hot liquor; and this plan is the better, although more difficult to regulate and carry through.

C. CONCENTRATING THE LIQUOR.—This is an operation of great importance in the pyritic lignite industry. The liquors measuring 27° to 28° Bé. have to be concentrated to 40° Bé. (measured hot); and when it is remembered that a cubic metre of cinder furnishes 600 litres of liquor, that this volume yields about 200 litres of residual water at 31° Bé., which has to be again concentrated, and so on, an idea will be gained of the volume of material to be treated, the amount of water to be evaporated, and the considerable weight of coal required for the operation. In fact the quantity of coal consumed in the production of 1200 tons of alum and 2500 to 3000 tons of ferrous sulphate is not less than 1500 tons, 1000 of which are required for the evaporation of the liquors.

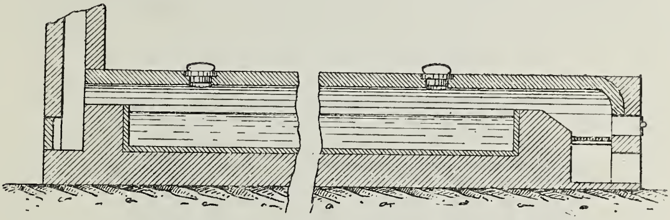


FIG. 124.—Reverberatory evaporating furnace for reduced liquor.

Not many attempts have been made to secure the proper utilisation of the fuel; and, in fact, the nature of the liquors to be treated, their acidity, the ease with which, under the influence of slightly prolonged heat, they deposit coherent sediments of gypsum, basic ferric sulphate, and dehydrated ferrous sulphate, all constitute difficulties hard to surmount.

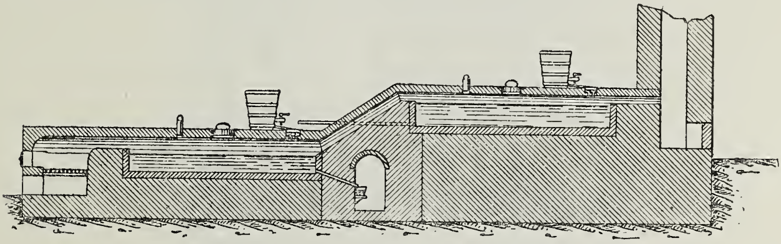


FIG. 125.—Double-bed evaporation furnace.

The reverberatory furnaces adopted in England have also been employed in France. In their simplest form they are very long in proportion to the width, and the bed takes the form of a dressed-stone basin to hold the liquor to be concentrated. The arch is greatly flattened, in order to compel the gases to circulate as near as possible to the surface of the liquid. In these furnaces the fuel is utilised in a fairly advantageous degree, their main drawback being the contamination of the liquors by ashes and soot.

Several improvements have been introduced, such as the combination of two evaporating basins with only one fire (see Fig. 125), the basin nearest the smoke-stack being on a higher level than the other, and serving as a preliminary heater. However, these furnaces have been superseded by leaden evaporat-

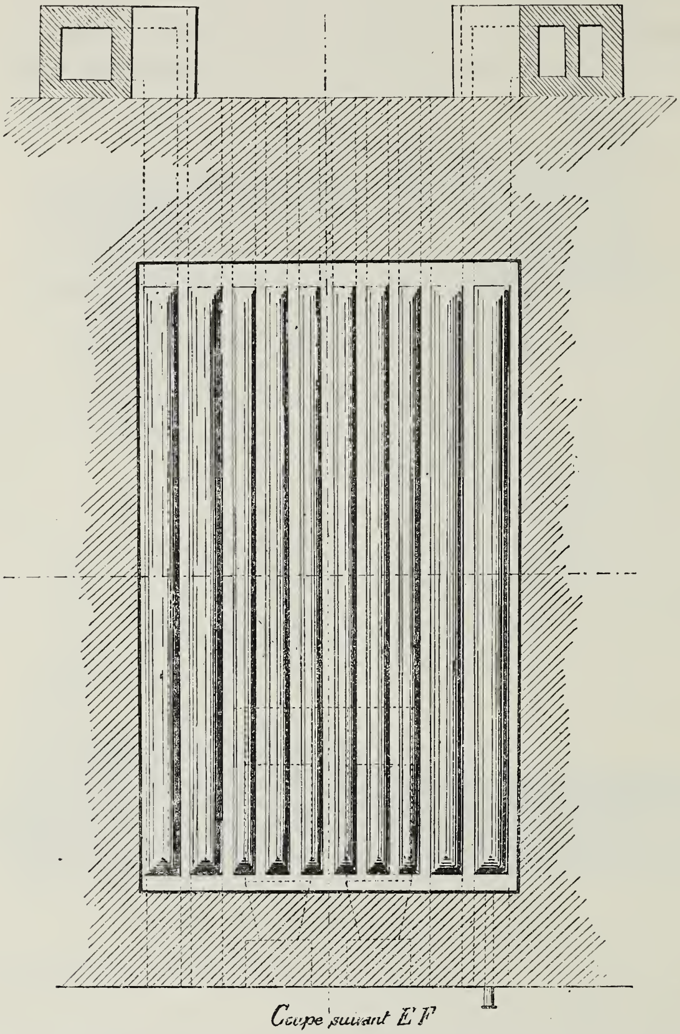
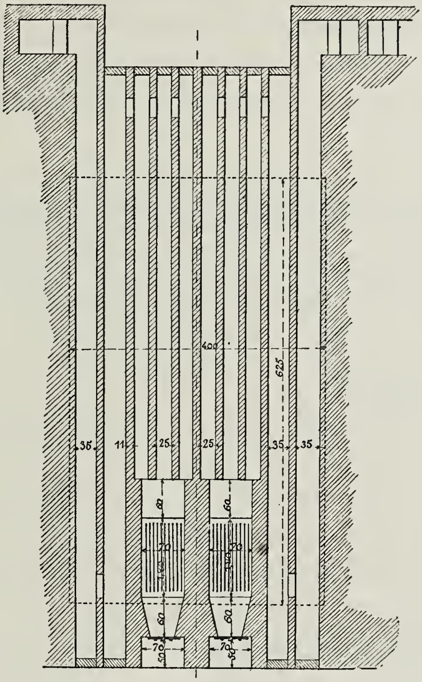
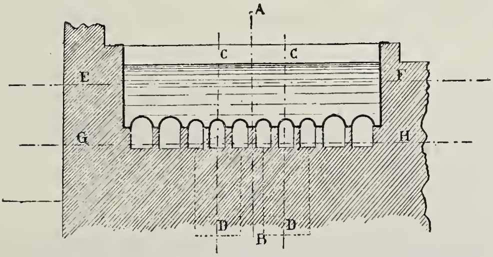


FIG. 126.—Section along EF. Leaden evaporating pan viewed from above, and showing the appearance of the bottom.

ing pans, which have the advantage of being inexpensive to keep in order, of being worth nearly their full value when broken up, and of keeping the liquors clean, though they waste heat in a deplorable manner, not more than 5 to 5½ lbs. of water being evaporated for 1 lb. of coal consumed.



(Section along GH.)



FIGS. 127 and 128.—Leaden evaporating pan. Plan and section showing details of firegrates and flues.

This defect is due—

(1) To the great thickness of lead necessary to preclude the

possibility of the walls getting out of shape under the influence of heat and the internal liquid pressure;

(2) To the low coefficient of conductivity of the metal;

(3) To the formation of incrustations of gypsum, basic ferric sulphate, and anhydrous ferrous sulphate;

(4) To the viscosity of the liquors to be concentrated;

(5) To the large superficial area of the liquor, favouring loss of heat by radiation.

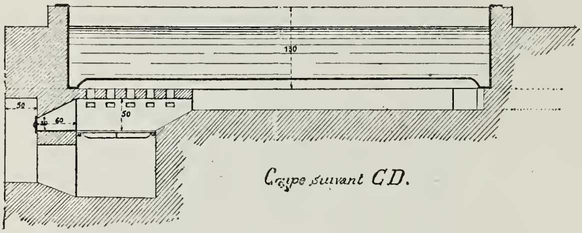


FIG. 129.—Leaden evaporating pan. Longitudinal section along CD.

These leaden pans are of variable dimensions. Those at Chailvet have an area of 25 square metres (270 square ft.), and are heated by naked flame. The direct impact of the fire is prevented by an arch, and the hot gases are led under the bottom of the pans, where they make a triple circuit through flues of masonry, the roofs of which flues are formed by undulations of the bed of the pan. The concentrated liquors are run off through gulleys, ordinarily closed by wooden plugs. The details of these pans, which are made of ½-inch sheet-lead, are given in Figs. 126 to 129.

At Chailvet an attempt was made at continuous evaporation in thin strata, the pans being arranged on the cascade system, as shown in Fig. 130.

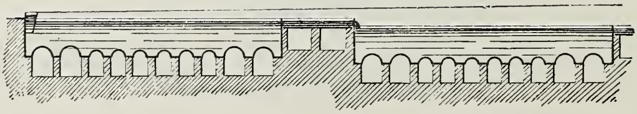


FIG. 130.—Leaden evaporating pans. Continuous system.

The endeavour had, however, to be abandoned, since after several hours' working there suddenly deposited—as the result of overheating—a heavy white sediment, which increased very rapidly, and set like plaster when removed from the pan. This salt proved to be none other than dehydrated ferrous sulphate ($FeSO_4, 4H_2O$), which, as we have seen, can be readily formed in the laboratory on subjecting a slightly acid, concentrated solution of ferrous sulphate to continued boiling.

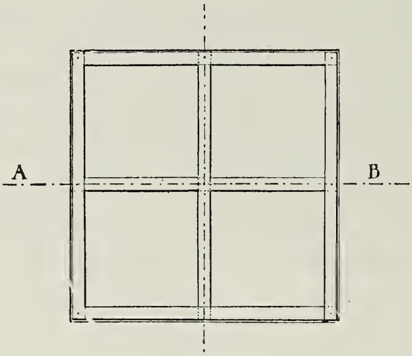
As soon as the liquor is concentrated it is run off into crystallising pans, holding 30 to 36 cubic metres (6600 to 8000 galls.), where it is left to cool. With three evaporators measuring 25 square metres (270 square ft.) in superficial area, and 1·20 metres (48 inches) in depth, about the above quantity of concentrated liquor can be delivered in 24 hours. The evaporators are kept in work for a period of 4 to 8 weeks at a time, after which they require cleaning out and repairing. As a rule they have to be entirely rebuilt every two years.

D. COST PRICE.—This, though very difficult to ascertain with exactness, under such varying conditions, may be estimated in an approximate manner as follows:—

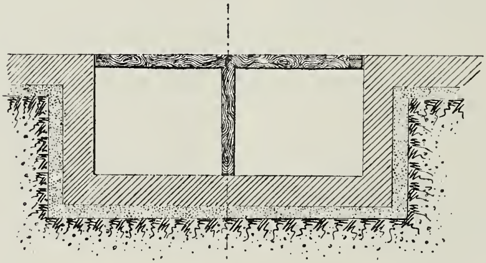
Receipts.		
27,720 lbs. ferrous sulphate at 1s.	277·2	shillings.
5500 galls. of crude alum liquor	274·8	,,
Total	552·00	shillings.

Expenses.		
Oxidised mineral	168·00	shillings.
Lixiviation	35·20	,,
Wear and tear of plant, tools; upkeep, oil, supervision	11·20	,,
Pumping and upkeep of pumps	12·80	,,
Coal, 5 tons at 14·4s.	72·00	,,
Cost of evaporation	32·00	,,
Sulphuric acid, 16 cwt. at 2·11s.	33·60	,,
Scrap-iron, 16 cwt. at 1·5s.	24·00	,,
General expenses and sundries	118·40	,,
Handling ferrous sulphate, packing, cartage	44·80	,,
Total	552·00	shillings.

E. CRYSTALLISING, PURIFYING, AND STORING THE FERROUS SULPHATE.—The crystallisers receiving the concentrated liquor are of dressed stone, coated externally with glaze and then with powdered chalk. They are embedded in the ground, and are provided with a lining formed, in the upper part, of an oak frame with cross beams, and, vertically, of wooden uprights. This arrangement is necessary to strengthen the walls, and, above all, to support the ferrous sulphate crystals which are deposited as the liquor cools. In order that the ferrous sulphate may keep when stored, it is necessary that the crystals should be deposited from a decidedly acid solution, since if the liquor is neutral or too feebly acid the crystals will not remain in merchantable condition, but oxidise and turn yellow owing to the formation of an incrustation of basic ferric sulphate. When the liquor is insufficiently acid, crystallisation proceeds in a very peculiar manner, the salt, instead of coming down in readily detachable granules, then crystallising as coherent plates of considerable hardness and very difficult to get out of the pans.



Plan.

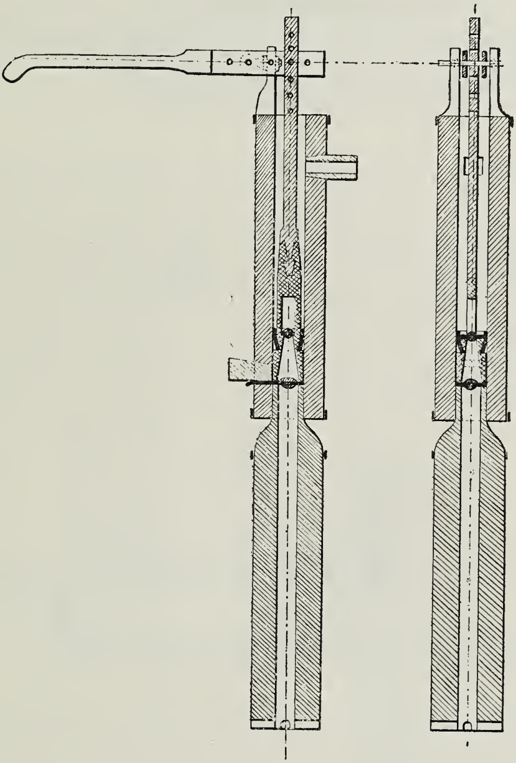


Coupe AB

FIGS. 131 and 132.—Plan and section of a dressed-stone crystallising vat. *Coupe* AB = section along AB.

In practice, endeavours are made to keep the liquor in a state of acidity corresponding to at least 10 grams of free H_2SO_4 per litre.

After a lapse of 20 to 25 days—for pans holding about 8000 gallons—the liquor will be cooled down sufficiently, and is then drawn off from the crystals by the aid of primitive wooden pumps, formed of two pieces, one fitting in the other. The lower and smaller piece is the suction pipe, whilst the larger, the barrel, contains a movable wooden piston, shod with leather to make a tight joint. The valves are also of leather, and are weighted with lead; their general arrangement is shown in Figs. 133 and 134. Pumps made of an alloy of lead and antimony have also been used, and, though more expensive in first cost, are cheaper to keep in repair than the wooden pumps, which soon get out of order.



FIGS. 133 and 134.—Details of wooden pump.

The decanted mother liquor is delivered into vats of thin sheet-lead, acting as refrigerators, and where a considerable extra amount of ferrous sulphate is deposited in the form of very small crystals. At Chailvet the cooling process is completed by running the liquors, as a thin layer, down a series of inclined planes, after which they are stored for working up into alum by the addition of ammonium sulphate.

The crystals are taken out by shifts of four men and transferred to a square receptacle fitted with a false bottom, on which a layer of brushwood is placed (Figs. 135 to 137). These receptacles are called "turbines," not because of any resemblance to the turbines or hydro-extractors used in sugar works, but probably through the similarity in the results obtained, though the real hydro-extractors are better. The crystals are washed with a saturated solution of ferrous sulphate, and left to drain for 12 hours: in this way they are gradually purged of aluminous mother liquor, and are soon ready for storage.

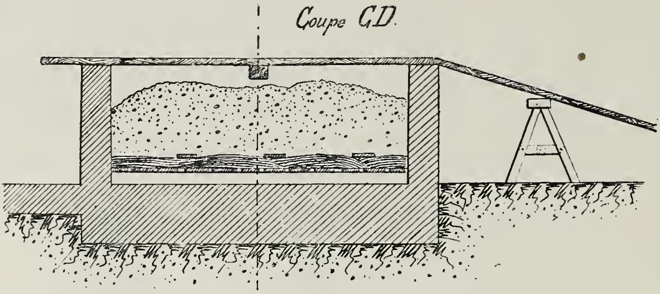


FIG. 135.—Longitudinal section (CD) of washing tank (turbine).

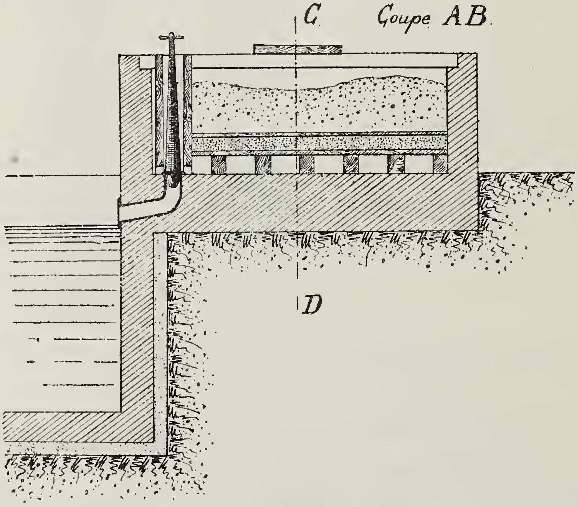


FIG. 136.—Transverse section of turbine.

This manufacturing process furnishes three commercial grades of the product:—

(1) The ferrous sulphate deposited on the bottom of the crystallising pans is in the form of very small grains, and is known as smalls (*petit-sel*), or by the letters PS. The weight per cubic metre (220 galls.) of this grade is about 1050 kilos. (21 cwt.) when loose, or 1250 kilos. (25 cwt.) when the heaps have settled.

(2) The crystals deposited on the walls and wooden fittings are larger, purer, and of a better colour. This grade is known as "ordinary copperas" (*couperose ordinaire*), or more simply O, and weighs, loose, 900 kilos. (18 cwt.) the cubic metre, or 1050 kilos. (21 cwt.) in the heap.

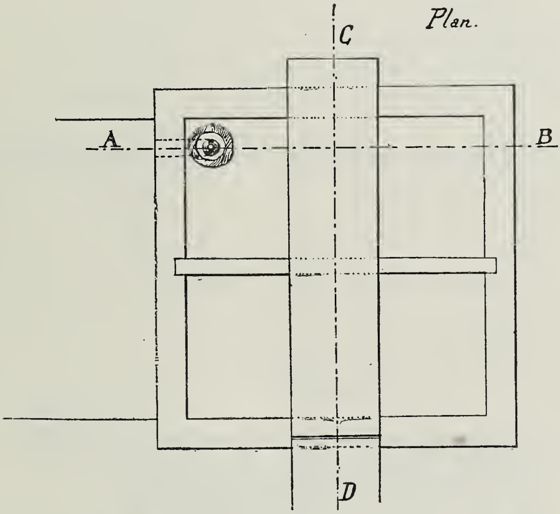


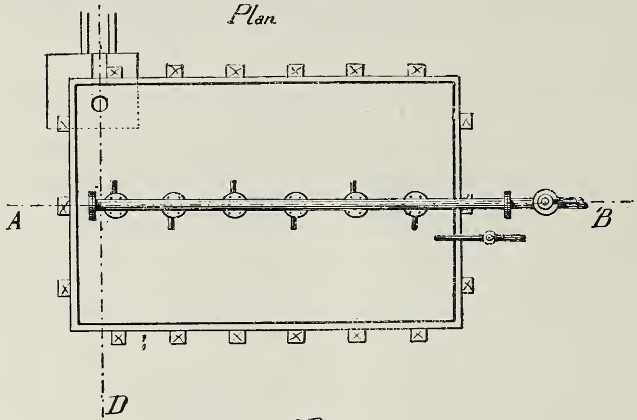
FIG. 137.—Plan of turbine.

(3) The very finely divided salt deposited as sediment in the cooling vats has to be left a very long time to drain, in the course of which it sets into blocks of a fair degree of hardness. To get it into merchantable condition it has to be carefully broken down by stamping on a boarded floor, and the resulting impure powder is known as crushed copperas (*couperose écrasée*). When drained the weight per cubic metre varies from 1350 to 1650 kilos. (27 to 33 cwt.), according to the fineness of division.

All these grades are somewhat impure, containing a small quantity of insoluble matter, calcium sulphate, ferric sulphate, a little free acid, water, and, above all, aluminium sulphate, carried down by the mother liquor disseminated among the crystals.

The PS grade contains an average of 86 to 88 per cent. of $FeSO_4, 7H_2O$.
,, O ,, ,, ,, 88 to 90 ,, ,,
,, crushed ,, only about 82 to 85 ,, ,,

Ferrous sulphate is placed on the market in bulk, bagged, or (more rarely) packed in casks.



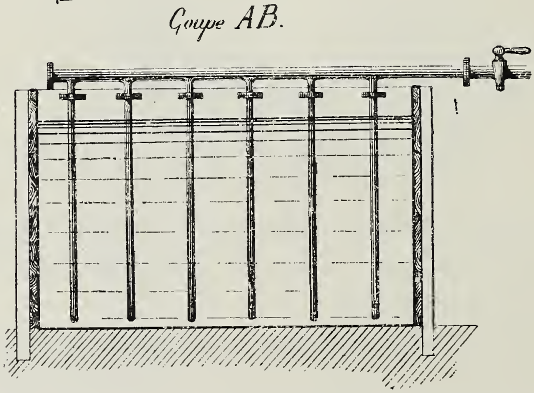


FIG. 138.—Plan. FIG. 139.—Longitudinal section along AB.
Re-crystallising vat.

F. RE-CRYSTALLISED FERROUS SULPHATE AND PSR.—Alum makers sell a purer grade of ferrous sulphate, containing at least 96 per cent. of the pure salt, and mainly used in dyeing. When in large crystals, this grade is termed re-crystallised copperas (*cuperose refonte*); and, when in crystals the size of Indian corn, is known as PSR (*petit sel refonte*), or re-crystallised smalls. These latter are obtained by re-crystallising the smalls in a leaden vat (Figs. 138 to 140) about the same size as the crystallisers, fitted with a spigot for running off the liquor, and heated by a jet of steam. The vat is first charged, about $\frac{1}{4}$ full, with clear water, or, better still, with a saturated solution of ferrous sulphate. Steam is turned on, and when the liquid is hot the crude crystals are shovelled in, the 42° to 44° Bé. solution thus obtained being run into a crystalliser. In order to obtain good results and prevent loss, certain precautions are necessary, namely:—Although, at the outset, solution may be effected at boiling heat, the temperature must be lowered in proportion as the concentration increases; and the injection of steam must be regulated so as to produce a temperature of 90° to 92° C. at the close of the operation. In the absence of this precaution the solution will be turbid as a result of the precipitation of dehydrated ferrous sulphate. Again, an interval of repose, from 1 to $1\frac{1}{2}$ hours, should be left between the completion of solution and the transfer of the liquor, in order to allow the heaviest impurities time to settle down. To obtain a maximum of large crystals, the crystalliser is provided with a large number of wooden rods, connected by bars, on which the

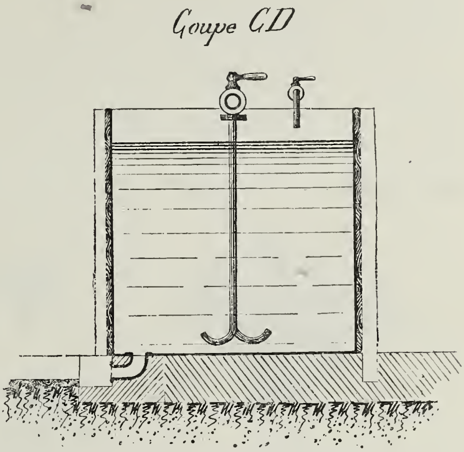


FIG. 140.—Re-crystallising vat. Cross section along CD.

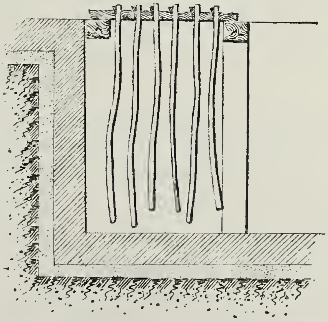


FIG. 141.—Re-crystallising vats, showing the arrangement of the rods destined to serve as nuclei for the crystallisation.

crystals form (see Fig. 141). The mass is left for 40 to 60 days, and, after the mother liquor has been run off, the salt is broken out, washed, and screened to separate the large PSR crystals. These grades are mainly packed in casks.

The residual mother liquor has a density of about 32° to 34° Bé., and is fully saturated with ferrous sulphate, containing also a notable quantity of aluminium sulphate, a little alum and free sulphuric acid, and traces of organic matter. In connection with this liquor a curious circumstance occurring within the author's experience may be mentioned here, namely, that when the re-crystallisation liquor has been left in the vats for some time, during the hot season, it becomes covered with a large number of small white spots, which gradually increase in size and turn grey, finally becoming of a greenish tinge, and covering the entire surface of the liquid with a scum $\frac{1}{5}$ to $\frac{1}{4}$ of an inch thick. On examining a portion of this film under the microscope, it was found to consist of closely interlaced mycelial filaments

FIGS. 142, 143, 144, and 145.

a, Mould collected on distillery waste; *b*, mould formed on re-crystallisation liquor; *c*, laboratory culture obtained by inoculating *b* on same liquor with addition of sugar; *d*, preparation obtained by sowing *b* on gelatinised meat broth.

floating in a liquid containing numerous small oval corpuscles resembling spores.

When re-examined after staining with Kühne's blue and being mounted in balsam, a number of sporiferous filaments, more or less branched, could be detected issuing from the mycelium, each branch carrying a cluster of sterigmata surmounted by chaplets of spores.

These peculiarities correspond to those of the most widely distributed mould known, namely *penicillium glaucum.* Laboratory cultures of this mould were easily obtained on meat broth, wherein it developed in 3 or 4 days. In re-crystallisation liquor, with or without an addition of sugar, growth was more protracted, requiring 15 to 20 days, and the resulting vegetation was invariably less vigorous and luxuriant than that obtained on meat broth. Attempts made to cultivate on the ferrous sulphate liquors the spores from a penicillium developing spontaneously on distillery waste resulted in failure, and it therefore seems as though the organism requires acclimatising before it will grow in a medium so rich in saline matter as the re-crystallisation liquor in question.

The same mould has also been encountered on media of very different composition,—water saturated with alum, fresh water rich in ferric sulphate, crude alum liquor; but on none of them in as vigorous condition as on re-crystallisation liquor. However this may be, the author regards the circumstance as too curious to be passed over in silence.

109. **Alum Manufacture.**—*A.* FROM THE RESIDUAL LIQUOR FROM THE FERROUS SULPHATE PROCESS (*brévetage* [*]).—The waste mother liquor from the crystallisation of ferrous sulphate (termed in French, *eau à bréveter*) is employed as raw material in the manufacture of alum. As a general thing it has a density of about 36° Bé., and contains aluminium sulphate, ferrous sulphate, a little ferric sulphate, and free acid, in the proportions indicated in the subjoined table, as well as a minute quantity of alum.

The preparation of alum from this liquor can be effected with

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[*] The origin of this term, which is currently used in French alum works, seems to be lost in obscurity. The process itself consists in treating waste ferrous sulphate liquor with ammonium sulphate.

the aid of various salts, such as potassium chloride, potassium sulphate, or ammonium sulphate. When, as at the present time, the price permits, this last-named salt may be advantageously used, being easier and more satisfactory to work with than potassium sulphate. Potassium chloride furnishes very poor results in point of yield, and, moreover, the mother liquors, charged with hydrochloric acid, have to be thrown away.

Constituents. Grams per litre.	1	2	3	4	5	6	7	8
Ferric sulphate ($Fe_2, 3SO_4$) . .	28·50	1·80	7·50	31·00	12·00	15·00	10·00	...
Ferrous sulphate ($FeSO_4, 7H_2O$) .	...	197·00	186·00	219·00	142·00	212·00	172·00	...
Aluminium sulphate ($Al_2(SO_4)_3$) .	292·00	225·00	206·00	264·00	256·00	250·00	250·00	352·00
Calcium sulphate ($CaSO_4$) . . .	...	...	...	...	1·00	9·00	7·00	...
Free sulphuric acid (H_2SO_4) . . .	...	...	...	...	...	...	10·00	...

The quantity of ammonium sulphate required in each case is determined by a laboratory experiment, conducted in the following manner:—

Fifty c.c. of the crude liquor are treated with 40 c.c. of pure water and 2 to 3 c.c. of sulphuric acid, followed by 7 grms. of ammonium sulphate, the whole being heated until complete solution is effected, and then allowed to crystallise. On the following day the mother liquor is decanted, the alum is washed with a saturated solution of alum, and is then dried and weighed.

More frequently the reduction test (*essai verdi*) is performed. This consists in treating 50 c.c. of the crude liquor with 40 c.c. of water and 3 c.c. of sulphuric acid, dropping in a few nails, and applying gentle heat, the evaporation of the liquid being prevented by covering the vessel with a sheet of glass. The nails are rapidly attacked, and as soon as the whole of the ferric sulphate has been reduced the excess of iron is removed and the liquid is treated with 7 grms. of ammonium sulphate, the remaining procedure being the same as in the first test. This method always gives results 0·5 to 1 grm. of alum lower than the other.

The amount of ammonium sulphate to be added in practice is deduced, by the aid of a special table, from the weight of alum obtained in the tests. Another, though less exact, method is by the cold precipitation—in a graduated tube—of a known volume of the crude liquor by a constant quantity of a saturated solution of ammonium sulphate, the precipitate being left to collect for some time, after which its volume is read off on the scale.

The table referred to is given below:—

I. In liberating a quantity of Aluminium Sulphate corresponding to 220 kilos. of Alum per cubic metre.				II. In liberating a quantity of Aluminium Sulphate corresponding to 200 kilos. of Alum per cubic metre.			
Weight of Alum from reduction test.	Ammonium Sulphate per cubic metre.	Weight of Ammonium Sulphate to be added per		Weight of Alum from reduction test.	Ammonium Sulphate per cubic metre.	Weight of Ammonium Sulphate to be added per	
		30 cub. m.	25 cub. m.			30 cub. m.	25 cub. m.
grms.	kilos.	kilos.	kilos.	grms.	kilos.	kilos.	kilos.
23·500	37·000	1100	925	22·000	33·500	1075	875
24·000	38·500	1150	950	22·500	37·000	1100	925
24·500	40·000	1200	1000	23·000	38·400	1150	950
25·000	41·400	1250	1025	23·200	39·000	1175	975
25·500	42·900	1300	1075	23·500	39·900	1200	1000
26·000	44·400	1325	1100	23·800	40·800	1225	1025
26·500	45·900	1375	1150	24·100	41·600	1250	1050
27·000	47·400	1425	1175	24·600	43·200	1300	1075
27·500	48·800	1475	1225	25·000	44·400	1325	1100
27·900	50·000	1500	1250	25·300	45·300	1350	1125
28·500	51·800	1550	1300	25·800	46·800	1400	1150
				26·000	47·400	1425	1175
				26·400	48·500	1450	1200
				26·700	49·400	1475	1225
				27·000	50·300	1500	1250
				27·500	51·800	1550	1300
				27·900	53·000	1600	1325
				28·600	55·000	1650	1375

In practice, if the liquors are rich enough, the indications on Table I. are taken. These figures relate to ammonium sulphate, and vary in the case of other crystallising reagents, as does also the theoretical yield obtainable. Thus—

100 parts by weight of KCl should theoretically furnish 636 parts of alum from the decomposition of 186·4 parts of ferrous sulphate, or the saturation of a corresponding quantity of sulphuric acid;

100 parts of K_2SO_4 should produce 544 parts of alum;

100 parts of $(NH_4)_2SO_4$ ought to yield 686 parts of alum.

The practical yield is, however, different. Thus, in using amounts of KCl and K_2SO_4 corresponding to 670 parts of alum, the quantities actually obtained were 451 with the chloride and 482 with the sulphate. The total alumina being represented by 56·6, the percentage recovered would be 86 per cent. in the former case and 92 per cent. in the latter.

In treating liquor with 51 per cent. of alumina the yield is as follows:—

Per 100 parts of pure potassium sulphate, 544 parts of alum (theoretical yield).

Per 100 parts of pure potassium chloride, 597 parts of alum.

In dealing with 54 per cent. in the same liquor, the yield of alum was 650 parts in the case of pure ammonium sulphate.

With potassium chloride 91 per cent. pure, the yield was—

In recovering the	86	per cent.	of the alumina,	496	parts alum.
,,	97	,,	,,	465	,,
,,	whole	,,	,,	458	,,

Since, as we shall see further on, in working with potassium chloride, the whole of the alumina has to be dealt with, it is easy from these data to compile a table of the weights of chloride to be added to the liquors, on the basis of the results obtained in the small scale experiments.

A similar table may, with equal ease, be drawn up for potassium sulphate, the following figures being taken as a basis:—

With	70	grms. of K_2SO_4,	380	grms. of alum	were obtained.
,,	80	,,	428	,,	,,
,,	100	,,	510	,,	,,

In the first case the 53 per cent. of the total alumina was dealt with, and the yield from the potassium sulphate was 543 parts (kilos.). In the second, the 60 per cent. of alumina was in question, and the yield amounted to 535 parts of alum; whilst finally, in the third case, the 71 per cent. of alumina was treated, but the yield was only 510 parts of alum.

For the alum recovery process the liquors are delivered into a dressed-stone tank, heated by steam passed through a number of leaden cylinders in the bottom of the tank, the general arrangement being that shown in Figs. 146, 147, 148. When the temperature of the liquid reaches 80° to 90° C. it is run off into crystallisers, ammonium sulphate being shovelled in during the operation. Solution proceeds rapidly under the influence of the heat, the baffles interposed for that purpose, and the use of suitable stirring paddles by the workmen; and, in proportion as the liquor cools, the alum crystallises out. Ammonium sulphate is by far the easiest reagent to use, since it is very soluble, the alum crystallises readily, the quantity of sub-salts formed is small, etc.; consequently this precipitant has much to recommend it.

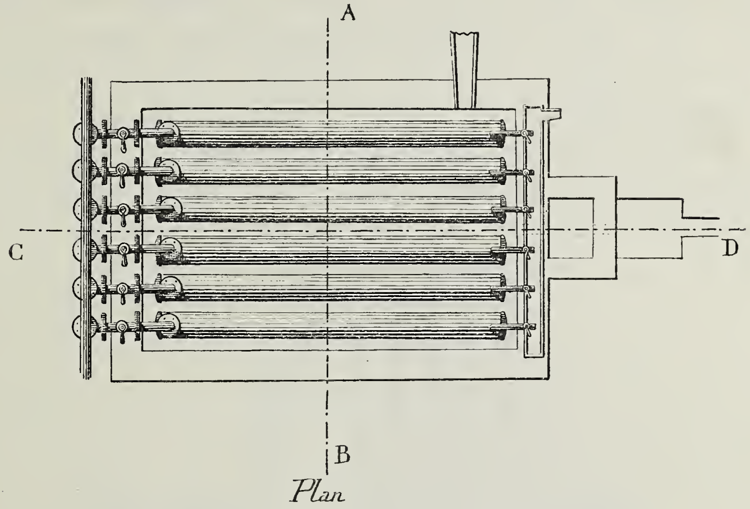

FIG. 146.—Plan of alum recovery tank.

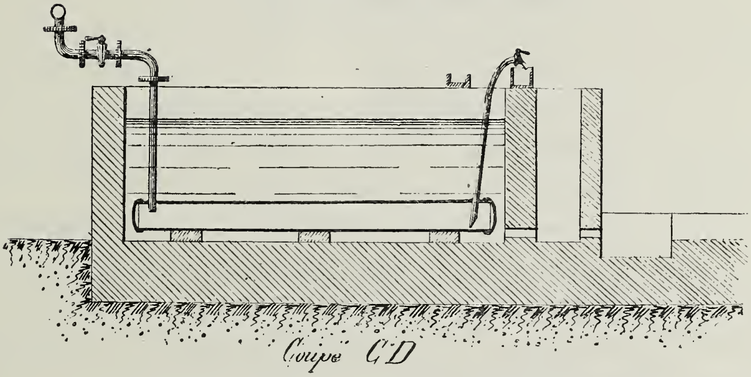

FIG. 147.—Longitudinal section (CD) of alum recovery tank.

On the other hand, potassium sulphate is more troublesome, owing to the formation of sub-salts, and consequent loss, during the precipitation and purification of the alum. Moreover, the relative insolubility of the precipitant causes difficulties, and it often happens that a portion remains undissolved and comes down with the alum, thus constituting another source of loss. The best plan, when potassium sulphate is used, is to dissolve it beforehand and add the solution to the crude liquor.

As for potassium chloride, this salt has little to recommend it, the loss in manufacture reaching as much as 25 per cent. Nevertheless, there are times when the use of this salt may prove economical, namely, when it can be had at a low price and ammonium sulphate is at prohibitive rates.

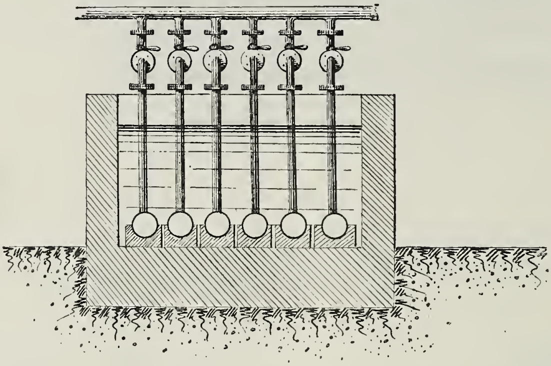

FIG. 148.—Alum recovery tank. Cross section along AB.

The residual mother liquor from the alum crystallisation is useless and has to be thrown away, the ferrous sulphate having been converted into chloride. Hence, to diminish the loss of alum, the liquor should be previously concentrated, so that its volume is reduced by one-tenth.

In order to obtain at one stroke the maximum yield of alum, the reverse of the procedure with potassium or ammonium sulphate is pursued, and the whole of the alumina in solution is dealt with.

It is easy to account for the advantage accruing from this method of working, the mother liquors being regarded as so much loss.

Take the following series of tests with 50 c.c. of crude liquor containing 80 grms. of alumina per litre:—

KCl added.	Alum obtained.	Loss.	Yield per 100 kilos. of KCl.
grms.	grms.	per cent.	kilos.
2·3	14·45	1·2	628
3·0	18·45	3·3	615
3·4	20·35	5·9	598
3·7	21·40	9·0	578

Suppose the price of the cubic metre (220 galls.) of crude liquor to be 16 frs. (12·8s.) and the cost of KCl 11 frs. (8·8s.) per cwt., the cost of the alum will work out as follows, allowance being made for the working expenses:—

	Cost of Crude Liquor.	Cost of KCl added.	Cost of Alum per cwt.
	shillings.	shillings.	shillings.
1st case	12·8	8·096	3·600
2nd ,,		10·560	3·160
3rd ,,		11·728	3·040
4th ,,		13·024	3·020

The method of treating the whole of the alumina, though irrational when potassium or ammonium sulphate is used, is therefore justifiable in the case of potassium chloride.

B. YIELD.—The insolubility of alum in its own mother liquor is merely comparative, and varies considerably according to circumstances. Of course it is a prime essential, in fact a *sine quâ non*, for obtaining a good yield, and conversely a minimum loss of ammonium sulphate, that the liquors treated should be concentrated and as highly charged with aluminium sulphate as possible. An equally important factor is acidity, and it is necessary that the liquor should contain at least 10 to 15 grms. of free H_2SO_4 per litre, the yield being deplorably poor when neutral liquors are treated.

The author tried the effect of neutralising a quantity of crude liquor with lime. After filtration, four samples, of 50 c.c. each, were taken, one of them being then diluted with 40 c.c. of pure water, whilst the others were mixed with 40 c.c. of acidified water so as to obtain a free acidity corresponding to 5, 10, and 20 grms. respectively of H_2SO_4 per litre. On being afterwards treated with 3 grms. of ammonium sulphate, representing 20·25 grms. of alum, the four samples gave the results set out in the following table:—

	1 Neutral Liquor.	2 Liquor with 5 grms. H_2SO_4 per litre.	3 Liquor with 10 grms. H_2SO_4 per litre.	4 Liquor with 20 grms. H_2SO_4 per litre.
Alum obtained .	15·040 grms.	18·00 grms.	18·40 grms.	18·450 grms.
Loss compared with theoretical yield	25·72 per cent.	11·11 per cent.	9·13 per cent.	8·88 per cent.

As we have seen, care is taken not to add sufficient ammonium sulphate to convert the whole of the aluminium sulphate in the liquor into alum, an amount of free aluminium sulphate equivalent to 200 to 250 kilos. (4 to 5 cwt.) of alum per cubic metre (220 galls.) of liquor being always left.

Actually, the solubility of the alum in its mother liquor decreases with the richness of the liquor in free aluminium sulphate, as the following table will show:—

	Experiment 1.			Experiment 2.		
	a	*b*	*c*	*a*	*b*	*c*
Ammonium sulphate employed	60	70	80	60	80	94
Corresponding amount of alum	411	480	548	411	548	644
Alum obtained . . .	370	415	440	397	488	524
Alum obtained, expressed in per cent. of ammonium sulphate . . .	616	593	550	662	610	557
Loss per cent. . . .	9·97	13·54	19·71	3·40	10·95	18·63

The presence of a small quantity of ferric sulphate is not injurious: if, however, the amount increases, and attains, for example, 30 to 40 grms. per litre, iron alum is formed, which contaminates the ammonium alum and entails a loss of ammonium sulphate.

Hydrochloric acid is injurious, its presence immediately reducing the yield to a considerable extent.

Two tests were made, one with 50 c.c. of pure water, the other with 50 c.c. of water containing 33 grms. of HCl per litre, each being employed to dissolve 20 grms. of pure dry alum, and then left at rest for 12 hours at a temperature of 6° C. The following results were obtained :—

	I Water.	II Water acidified with HCl.
Alum employed	20 grms.	20 grms.
Alum crystallised out	17·210 ,,	14·480 ,,
Loss	5·58 per cent. referred to the water.	11·04 per cent. referred to the acidified water.

The same applies to chlorides, an experiment made, under the same conditions as the preceding ones, with 50 c.c. of water and 20 grms. of alum, but with an addition of 10 grms. of NaCl, having given only 15·770 grms., *i.e.* a loss of 8·46 of alum per 100 of water.

This influence of hydrochloric acid explains the poor results obtained in the manufacture of alum by the aid of chlorides. Thus, if 50 c.c. of alum liquor be treated with equivalent quantities of ammonium sulphate and ammonium chloride, the following results are obtained :—

	I With $(NH_4)_2SO_4$.	II With NH_4Cl.
Alum	27·500	23·500
Shortage with NH_4Cl	...	4·000

In the same manner with potassium chloride :—

	I With K_2SO_4.	II With KCl.
Alum	32·7	30·3
Shortage with KCl	...	2·4

The alum recovery process is therefore a delicate operation, and requires care in its performance.

C. COST PRICE.—The remarks made in connection with the ferrous sulphate process are also applicable here. Nevertheless, the cost of the alum recovery process may be approximately determined as follows :—

Receipts.

Alum in crude liquor .	7425 kilos.	
Loss [*]	825 ,,	
Alum recovered .	6600 kilos. = 13·2 cwt. at 3·176s.	= 419·20 sh.
15 cub. m. (3300 galls.) of liquor returned for evaporation		= 120·00 ,,
Total . . .		539·20 sh.

Expenses.

25 cub. m. (5500 galls.) of crude liquor . . .	274·80 sh.
Ammonium sulphate, 22 cwt. at 10s.	220·00 ,,
Coal, 1 ton at 14·4s.	14·40 ,,
Labour, pumping, maceration of alum, etc. . . .	30·00 ,,
Total . . .	539·20 sh.

110. **Purifying the Alum.**—*A.* TREATMENT OF THE CRUDE ALUM.—*Production of Ordinary Alum.*—When the liquor in the crystallisers has cooled down sufficiently, *i.e.* at the end of 15 to 20 days, the mother liquor is drawn off and run through a series of baffles, in order that it may finish cooling and deposit the little alum it still contains; it is then returned to the evaporators. This mother liquor has a density of about 32° Bé., and, in addition to a little alum, contains ferrous sulphate, aluminium sulphate, and a small quantity of ferric sulphate, the composition being shown in the following table :—

Substances present. Grms. per litre.	1	2	3
Ferrous sulphate ($FeSO_4$, $7H_2O$) . .	276·00	223·00	223·00
Ferric sulphate ($Fe_2(SO_4)_3$) . . .	6·30	4·00	4·50
Aluminium sulphate ($Al_2(SO_4)_3$) . .	116·00	143·00	170·00

The crude alum, deposited as brownish crystals on the walls of the crystallisers, is chipped out and wheeled off to a special tank fitted with a wooden false bottom (see Fig. 149).

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[*] On comparing the recovered weight of alum with the theoretical yield of the liquor, it is seen that a discrepancy exists, and that the loss is considerable. This loss is due to the solubility of the alum, part of which is retained by the crude liquor and part removed by the mother liquor in the course of washing. The amount of loss varies, of course, according as the work is well or ill done, and also according to the number of re-crystallisations to which the alum is subjected. Thus, where half the product is to consist of purified alum, and the remainder of ordinary alum (*alun de glace*), the loss under favourable conditions fluctuates between 9 and 12 per cent. of alum, referred to the ammonium sulphate employed. In the above calculation the loss is taken as 11 per cent.

Here it is washed three times in succession with saturated solutions of alum, the cleanest being used last, and is left to drain after each washing. The solution employed for washing is obtained from the re-crystallising process, and contains 80 to 90 kilos. (175 to 200 lbs.) of alum per cubic metre (220 galls.), together with a little ferrous sulphate. When it has been used several times and becomes too impure to serve longer it is returned to the lixiviation tanks, where it is mixed with weak liquor.*

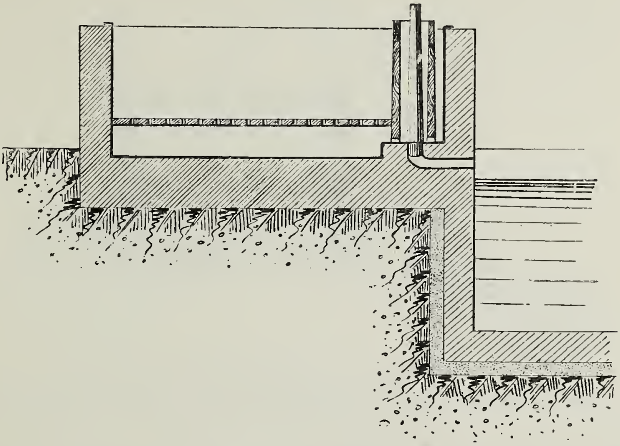


FIG. 149.—Washing and draining tank for alum.

No. of Test.	Moist Alum.	Dry Alum.
1	100	81·5
2		82·2
3		80·4
4		77·2
5		83·0
6		83·7
7		77·0
8		82·4
9		80·0
Mean .	...	80·8

The washing process eliminates most of the mother liquor adhering to the crystals, and the small amount of ferrous sulphate

---

* Sometimes it is concentrated for the recovery, by crystallisation, of part of the contained alum. Owing to the large consumption of coal involved, this plan has little in its favour, though occasionally it may be resorted to with advantage.

which has crystallised with the alum. It may be useful to approximately determine the weight of pure alum corresponding to a given quantity of alum washed and drained in this way. This weight is, of course, variable, but within such narrow limits that its empirical determination is not difficult. The preceding figures are obtained from tests made with moist alum simply drained.

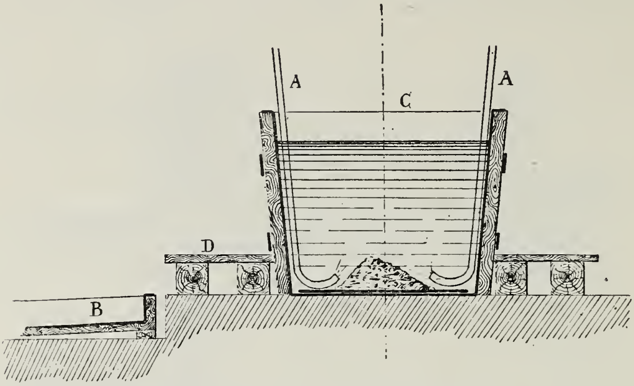


FIG. 150.—Alum re-crystallising plant.
C, Vat; A, steam pipe; D, wooden platform; B, trough delivering the alum solution to the block moulds.

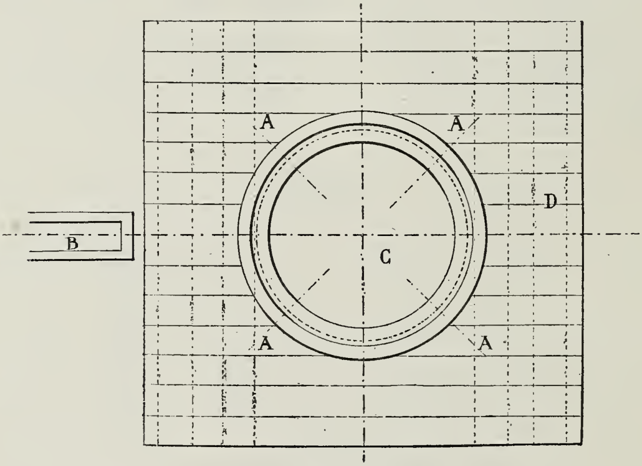


FIG. 151.—Plan of vat C.

It may therefore be considered that 100 parts by weight of moist alum, simply drained, correspond, on the average, to 81 parts of dry alum.

This alum, however, is not yet pure enough for sale as it is, and, moreover, is not in a merchantable form. It therefore must be re-crystallised a second time, and for this purpose is re-dissolved by the aid of direct steam, in special vats, generally of lead, slightly wider at the top than the bottom, and fitted with a false bottom of pumice or thick sheet-lead.

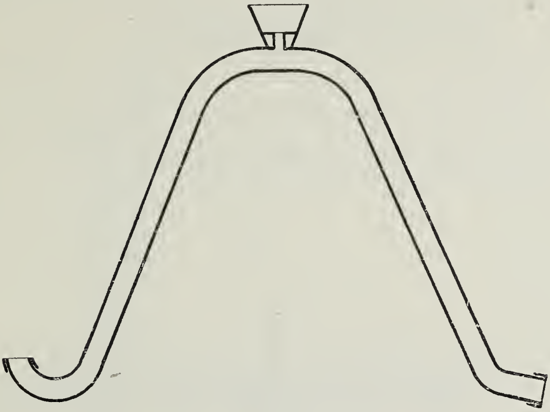


FIG. 152.—Copper syphon.

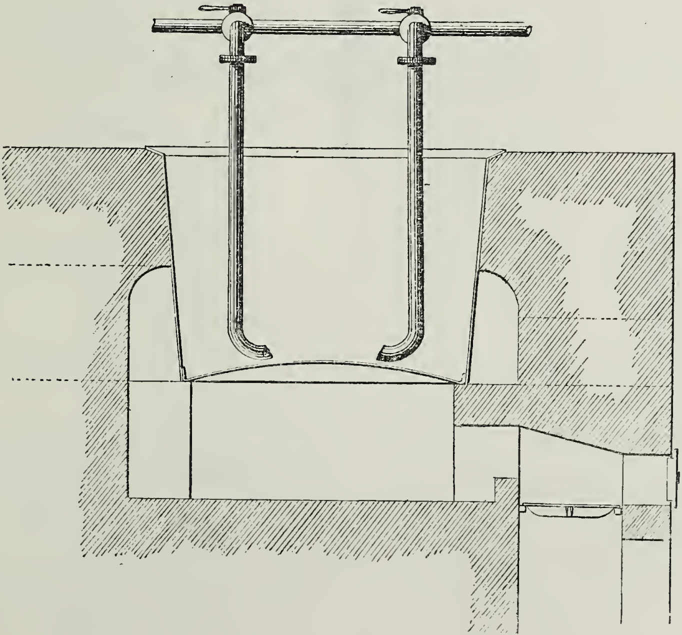


FIG. 153.—Copper vat with underneath fire.

The steam pipes extend nearly to the bottom of the vat, and are bent slightly upward at their lower extremity (Figs. 150, 151). The solution is drawn off through a copper syphon, shown in Fig. 152.

Formerly copper vats, heated by a fire underneath, were used, the steam jets being also employed (see Fig. 153), a plan which enabled more highly concentrated solutions (43° to 44° Bé.) to be obtained.

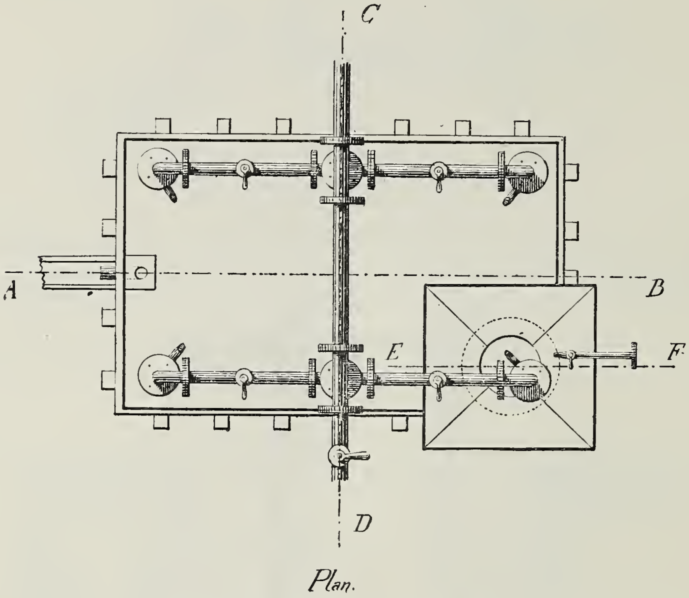


FIG. 154.—Large alum tank. Plan.

The capacity of the vats is such as to nearly correspond to a block of alum, *i.e.* about 440 to 550 gallons.

Sometimes the vats are replaced by large tanks of thin sheet-lead, strengthened with wood, and of sufficient dimensions to contain as much as eight blocks—16 to 20 tons—of alum. In such event, the alum, instead of being thrown direct into the vat itself, as is the usual practice—the steam jets producing sufficient agitation—is placed in a kind of hopper discharging into a perforated cylinder, in the interior of which a steam pipe sets up an energetic agitation. This appliance is generally mounted in one corner of the tank (see Figs. 154, 154A, 155).

The *modus operandi* in any case is as follows:—Enough alum is thrown in to cover the mouths of the steam pipes.

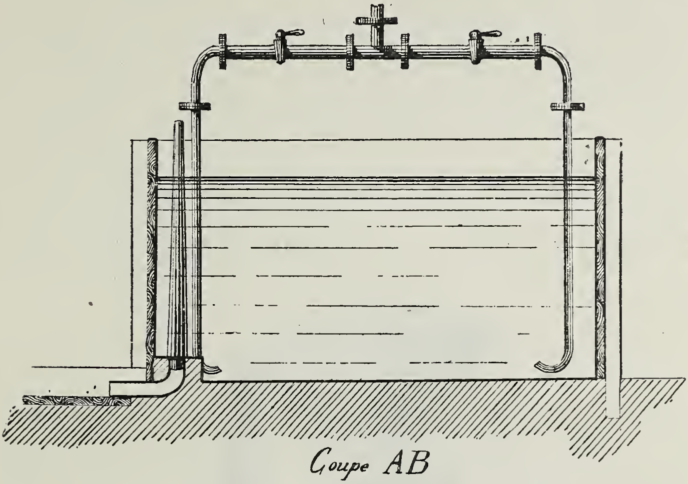


FIG. 154A.—Large alum tank. Section along AB.

Steam is then turned on, and more alum is added in proportion as solution progresses. When the vat is full, steam is shut off and the mass is left at rest for about an hour, so as to allow the

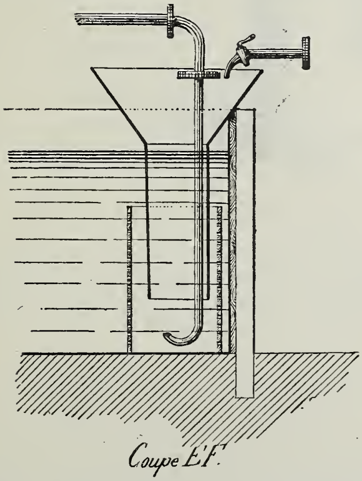


FIG. 155.—Apparatus for introducing the alum. Section EF.

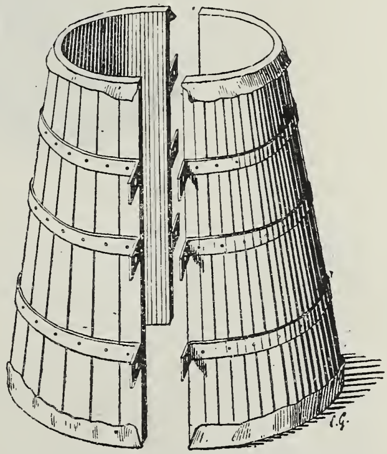


FIG. 156.—Block mould for alum.

insoluble matter to settle down. The density of the solution is 40° to 41° Bé. in the case of leaden vats heated solely by steam, and 43° to 44° Bé. in copper pans with steam and fire heat.

When the liquor is sufficiently clear it is drawn off through a copper syphon and delivered to the block moulds. The large leaden tanks are emptied by means of an outlet pipe, about 8 inches from the bottom, and usually closed by a wooden plug.

The block moulds, which vary in size at different works from 440 to 550 gallons, are in the shape of a truncated cone (Fig. 156), and are formed of two or three sections, made of oak staves joined together with iron hoops and lined with thin sheet-lead. The joints are tightened by fastening the hoops together by means of bolts and nuts and rubber plates. Around the base of the mould a luting of clay makes a tight joint with the boarded floor of the room.

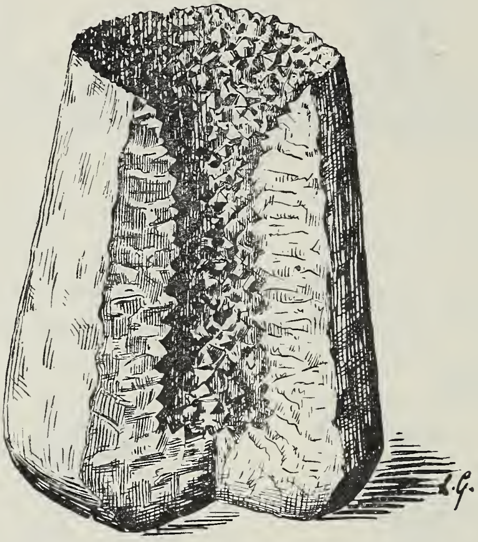


FIG. 157.—Block of alum cut open to show the interior.

The mould thus prepared and filled with the alum solution is left to cool. The alum rapidly crystallises on the sides and bottom, and at the end of about a week the mould can be taken apart, exposing the block of alum (Fig. 157), which is left several days longer, 15 to 20 days being required to effect thorough cooling. At the end of this period the walls of the block will be 10 or 12 inches thick, the central cavity containing 90 to 100 gallons of mother liquor in a 2-ton block. This mother liquor measures 5° to 6° Bé., is drawn off by boring a hole in the block, and is sent into storage tanks, from which it is afterwards withdrawn for washing the crude alum. When too impure it is used in the lixiviation process or returned to the evaporators, being preferably concentrated separately, and not mixed with the fresher liquors.

The block alum is cut into large lumps with the axe, and these in turn are broken down to about the size of a man's fist, the product then constituting the ordinary alum of commerce. Only the portion from round the sides of the mould can be regarded as merchantable alum; together with that part of the base which is of a greyish colour, owing to the presence of impurities, and which, under the name of "grey alum," meets with a ready sale to curriers; and the best of the broken smalls, which are passed through a mill and sold as "crushed alum";—the rest, consisting of the foot of block, which is laden with clayey impurities, and of the dirty fragments, having to be purified to fit it for sale.

The block of alum obtained from 2200 parts by weight of crude alum furnishes, on the average—

Ordinary lump alum	1000 parts.
Crushed alum	260 ,,
Waste for re-purification (½ AE)	600 ,,
Grey alum	300 ,,
Alum left in mother liquor	40 ,,
	2200 parts.

The smalls can be crushed by hand with a heavy pounder on a block of stone, or passed through a crushing mill consisting of a core of fluted steel turning inside a fluted crown (see Fig. 158).

Alum is also sold in the form of fine powder, ground in special mills.

B. MANUFACTURE OF PURIFIED ALUM. — For certain branches of the dyeing industry a purified alum almost exempt from iron is required—one, namely, that gives practically no blue coloration with prussiate. Such a product may be obtained by re-crystallising the ordinary alum in the same manner as in preparing that quality from crude alum. It is also prepared from block alum smalls, this dirty, greyish, and sometimes muddy waste being re-dissolved by steam in a large leaden vat similar to those already described as being used for dissolving crude alum (8 blocks at a time).

The operation is continued until a 28° to 30° Bé. liquor is obtained, this being then covered up to prevent loss of heat, and left until the next day. The clear liquor is run into a crystalliser, whilst the turbid residue, which still contains a notable quantity of alum—chiefly as sub-salts—is extracted by one or two washings with hot water and thrown away. When potassium sulphate has been used to form the alum, the loss in the form of insoluble sub-salts thrown away with the turbid residue is much greater, but may be diminished by a treatment with sulphuric acid.

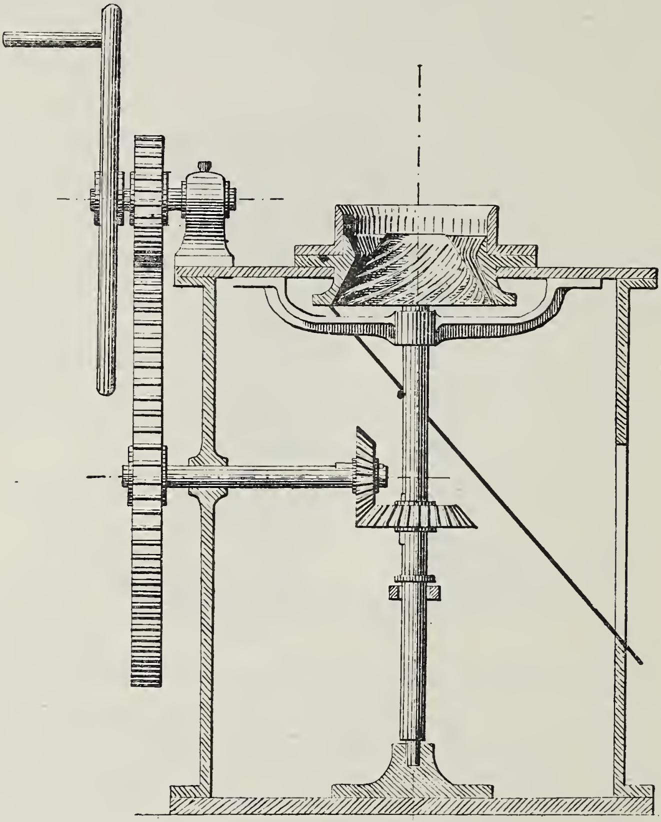


FIG. 158.—Alum mill.

The liquor is decanted and the alum drained, after which it is re-crystallised into blocks of semi-purified ($\frac{1}{2}$ AE) alum, in the manner already described. These blocks are broken into masses the size of a man's head, and, when re-crystallised in copper vats, furnish blocks of purified alum (AE), which are broken into nuts, any dirty pieces being set aside and the remainder washed to complete the purification. With this object, the alum, prepared in the manner just described, is spread out, as uniformly as possible, in boxes fitted with false bottoms. It is then covered with a very pure solution of alum and left for 12 hours, after which the liquid is drained off into a receptacle underneath, and the alum re-washed with pure water.

It is next taken out of the boxes, spread out to dry on sloping tables freely exposed to the air, or in shallow wicker sieves (Fig. 159), and is then ready for sale.

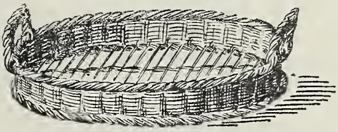


FIG. 159.—Wicker sieve for drying purified alum.

As will be evident, the production of purified alum is a very expensive process, the cost being considerably augmented by the great amount of labour entailed in the successive re-crystallisations, and by the loss of material ensuing from these operations.

C. COST OF PRODUCTION.—The following tables show the mode of estimating the cost of each set of operations comprised in the purification of alum :—

(1) *Ordinary Block Alum.*

Receipts.

Lump, crushed, and grey alum :—

Lump and crushed alum	25·2 cwt.	at 4·089 sh.	= 103·04 sh.
Grey alum	6·0 ,,	,,	= 24·55 ,,
Residue for re-crystallisation	12·0 ,,	2·635 ,,	= 31·61 ,,
Total	43·2 cwt.		= 159·20 sh.

Expenses.

Crude alum, 44 cwt. at 3·181 sh.	= 140·00 sh.
Alum left in solution, 0·8 cwt. (reckoned with the loss in recovery)	...
Coal, 2·0 cwt. at 0·72 sh.	= 1·44 ,,
Wear and repair of pans, etc.	= 1·76 ,,
Labour in re-crystallising	= 2·00 ,,
Wear and repair of moulds	= 2·00 ,,
Cartage, packages, labour, etc.	= 12·00 ,,
Total	= 159·20 sh.

(2) *Re-crystallising for ½ AE Grade.*

Receipts.

Alum obtained, 88 cwt. at 3·882 sh.	= 341·60 sh.
Total	= 341·60 sh.

Expenses.

Smalls for re-crystallising 12 cwt. at 2·636 sh.	= 316·32 sh.
Alum water, 1760 galls.	= 3·20 ,,
Coal, 14 cwt. at 0·72 sh.	= 10·08 ,,
Loss of alum (reckoned with recovery)	...
Labour, upkeep, etc.	= 12·00 sh.
Total	= 341·60 sh.

(3) *Block Alum, ½ AE Grade.*

Receipts.

Alum to re-crystallise as AE,	30·0 cwt.	at 3·883 sh.	= 116·48 sh.
,, ,, ½ AE,	13·2 ,,	3·540 ,,	= 46·72 ,,
Total	43·2 cwt.		= 163·20 sh.

Expenses.

Alum for ½ AE,	32 cwt.	at 3·883 sh.	= 124·16 sh.
Smalls	12 ,,	2·636 ,,	= 31·64 ,,
Coal	2 ,,	0·72 ,,	= 1·44 ,,
Labour, upkeep, etc.			= 5·96 ,,
Total			= 163·20 sh.

(4) *Block Purified Alum.*

Receipts.

21 cwt.	purified alum	at 5·742 sh.	= 120·56 sh.
16 ,,	alum for re-crystallising	,, 4·035 ,,	= 64·56 ,,
4·2 ,,	,, ,, to ½ AE	,, 3·586 ,,	= 14·88 ,,
41·2 cwt. alum	Total		= 200·00 sh.

Expenses.

Ordinary alum,	16·54 cwt.	at 4·088 sh.	= 67·68 sh.
Alum, ½ AE	27·46 ,,	3·88 ,,	= 106·48 ,,
Coal	2 ,,	0·72 ,,	= 1·44 ,,
Labour, upkeep, etc.			= 6·00 ,,
Crushing, washing, drying, etc.			= 6·40 ,,
Cartage, packages, etc.			= 12·00 ,,
Total			= 200·00 sh.

D. GENERAL MANUFACTURING ACCOUNT.—It is difficult to draw up statements showing the cost of any one operation in more than an approximate manner, though the general account given below will furnish an exact idea of the total results of working the alum recovery process, based on an output of 1500 tons per annum. Of course the balance will vary one way or the other, according to the deviation from this figure, since some of the factors, such as general expenses, horse-keep, etc., being within a certain limit invariable for the whole year, will have to be apportioned to a larger or smaller quantity of material treated.

Manufacturing Account, per cubic metre (35·3 *cubic feet*) *of Mineral treated.*

Expenses.

Mineral (extraction, sundry expenses)	1·600 sh.
Horse-keep	0·360 ,,
Upkeep of plant	0·800 ,,
Timber, cooperage, etc.	0·304 ,,
Labour	3·040 ,,
Ammonium sulphate	3·600 ,,
Sulphuric acid	0·560 ,,
Scrap-iron	0·320 ,,
Coal	1·600 ,,
Bags	0·336 ,,
General expenses	1·880 ,,
Total	14·400 sh.

Receipts.

Ferrous sulphate	4·2 cwt. at 1·105 sh.	4·64 sh.
Alum, ordinary and purified,	2·2 ,,	11·36 ,,
	Total	16·00 sh.

Balance.

Receipts	16·0 sh.
Expenses	14·4 ,,
Profit	1·6 sh.

111. **Construction and Upkeep of Plant.**—The treatment of lignites, as also the bauxite, alunite, and many other chemical industries, entails the use of numerous leaden vessels and appliances, which need frequent repair. In works dealing with the treatment of lignites a lead worker's shop is an indispensable part of the establishment. Here are moulded the large sheets of lead required for constructing the various pans, the necessary soldering is performed, and other repairs executed.

The production of leaden plates of a certain thickness is comparatively easy. The plant is simple, consisting of a cast-iron melting pot—fitted with pouring spout (see Figs. 160 and 161) closed by a stopper—and of a shallow bed, or table with raised edges, to contain the layer of sand on to which the molten metal is poured. The method of working is as follows: The old metal to be re-cast is melted down in the iron pot, the casting bed being meanwhile prepared by spreading over the table a uniform layer of wet sand, which is pressed down to a suitable degree, smoothed by means of copper trowels, and allowed to dry slightly. When the lead has been melted down, the pouring spout is opened—the stopper has been kept cool by a stream of water so as to form a leaden plug in the mouth—and the molten mass is poured into a sheet-iron pot, fitted to the casting bed, and capable of being tilted up at one end by means of suitable levers.

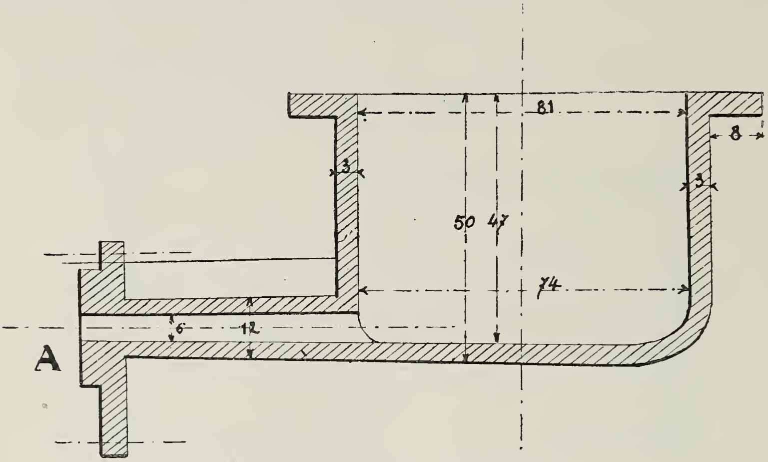


FIG. 160.—Cast-iron pot for melting lead.

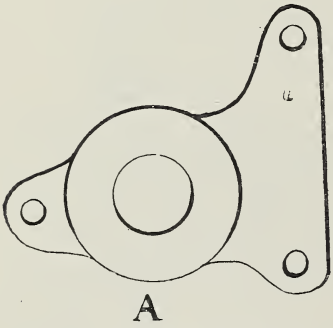


FIG. 161.—Front view of pouring spout.

The lead to be cast must be neither too hot nor too cold, and it is in this second pot that the metal is left to attain the right temperature, which is determined in an empirical manner—namely, as soon as the metal begins to solidify round the sides it is considered ready for casting; whereupon the pot is tilted and the metal flows over the sandy bed, the raised edges of the table preventing it escaping at the sides.

The metal is distributed uniformly over the bed by means of a wooden levelling bar, whose ends slide along the table edges, and the breadth of which enables the thickness of the cast sheet to be regulated according to requirements. All that is then necessary is to leave the sheet to cool down, and cut it up as required.

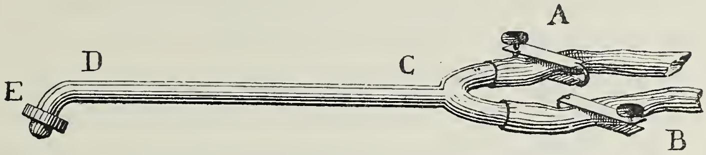


FIG. 162.—Blowpipe for *autogène* soldering.

The joints are soldered by the *autogène* method invented by Desbassyns de Richemond, a process which, when performed by good workmen on clean surfaces, furnishes joints more solid, by reason of their great thickness, than the sheets of lead themselves.

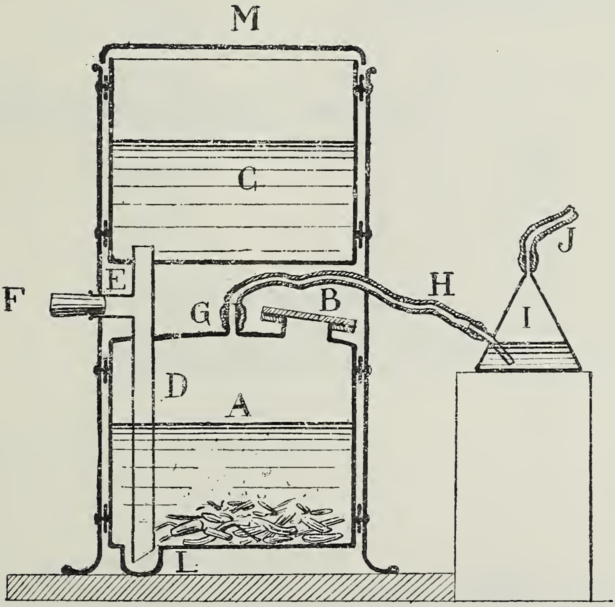


FIG. 163.—Leaden hydrogen generator for the *autogène* soldering process.

The work is done by the aid of a blowpipe (Fig. 162) supplied with air and hydrogen through two caoutchouc pipes fitted with stopcocks A and B. The gases are mixed in the part CD, which carries a movable ajutage E; and by means of the cocks A and B the dimensions of the flame can be controlled by the workman, and an excess of hydrogen maintained so as to preserve the reducing character of the flame.

The hydrogen is furnished by a leaden generator (Fig. 163), the lower chamber of which (A) is charged with scrap-iron through the capped tubulus B. The upper chamber C, which is covered with a loose leaden plate M, contains dilute sulphuric acid, and communicates with A by means of the pipe D, which dips into a cup L. The pipe D is provided with a branch E, which is closed by a plug F while the apparatus is in work. The hydrogen generated in A escapes through the neck G into a pipe H, which discharges it through the water in the bottle I, the neck of which (J) communicates with the blowpipe supply tube. The bottle is interposed to prevent any flashing back of the gas from the blowpipe to the generator.

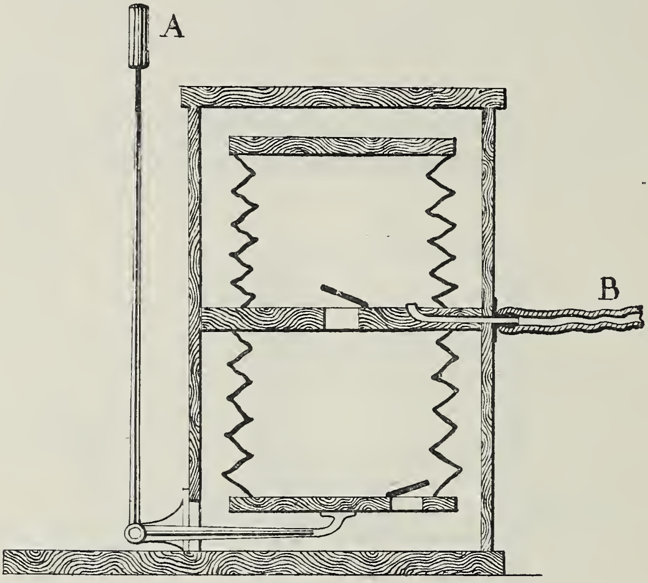
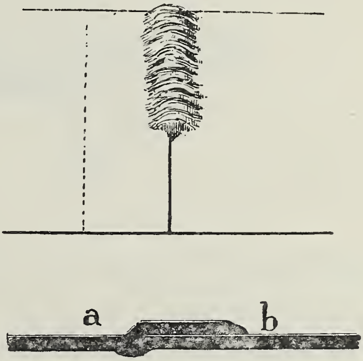


FIG. 164.—Bellows.

On ceasing to use the blowpipe the workman closes the stopcock of the hydrogen pipe, whereupon the pressure of gas in A increases and forces the acid up through the pipe D, away from contact with the iron filings, and consequently the evolution of gas is discontinued automatically.

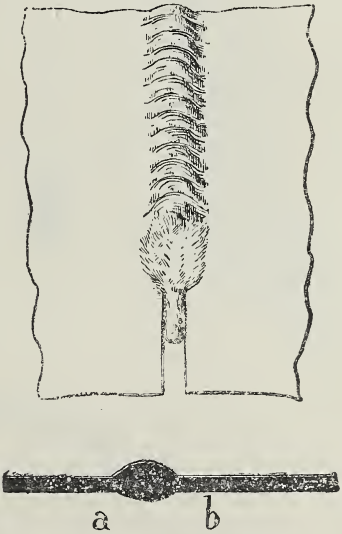
To empty the generator, the plug F is taken out, the blowpipe cock being kept turned off.

The air blast required to support the hydrogen flame is supplied by the bellows shown in Fig. 164, the lever A being worked by an assistant seated on the bellows case. The blast is discharged from the bellows through the neck B.



Figs. 165, 166.—Soldered lapped butt joint in leaden sheets.

Whenever possible the work should be done on the flat, the ends of the two sheets to be joined being lapped over about 1¾ to 2 inches (Figs. 165, 166), the contact surfaces *a* and *b* scraped clean, and the metal of the upper sheet melted by the blowpipe flame and united with the under sheet. A simpler method is to simply put the two edges (butts) of the sheets together (Figs. 167, 168) and run the blowpipe jet along the space between *a* and *b*, so as to melt the metal and join the two sheets; this joint, however, is not so strong as the lapped joint. In both cases it is advisable to hold in the blowpipe flame a stick of solder, which fuses and increases the thickness of the joint.



Figs. 167, 168.—Butt joint.

The work of soldering lead sheets is a delicate operation, and requires skilled labour. If the blowpipe jet be directed too long on the same spot, the sheet is liable to melt through and form a hole; consequently the flame must be shifted the moment the solder is sufficiently hot to begin to melt and fuse with the metal of the under sheet. In the case of thin sheets the task becomes particularly delicate, and great dexterity is required to ensure success.

Again, the soldering of upright sheets is very difficult. In this case use is made of the small wrought-iron tool, shaped like a gouge, shown in Fig. 172. The work of soldering is begun at the bottom, and, a stick of solder being laid on the tool, the latter is held against the edges of the two sheets, the flame being then directed alternately against the solder and the parts to be joined.

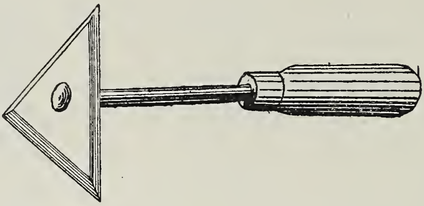
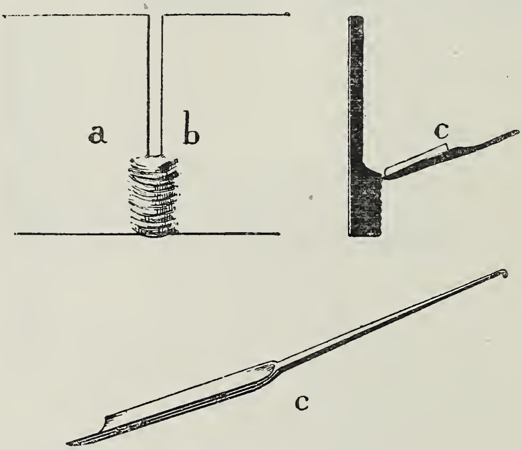


FIG. 169.—Scraper for brightening the parts to be soldered.



FIGS. 170, 171, and 172.—Soldering a vertical joint.

The solder melts, runs down to the lip of the tool and there solidifies, thus joining the edges of the leaden sheets. The tool is then raised about $\frac{1}{24}$ or $\frac{1}{12}$ of an inch higher up, and the same process is repeated until finally a ridge is formed all the way up uniting the sheets (Figs. 170, 171).

A good workman can solder sheet-lead of about ½ an inch thick at the rate of 40 to 60 inches an hour on the flat, or 12 to 16 inches of upright work.

In the case of thin sheets, a practised hand can solder at the rate of $6\frac{1}{2}$ to $7\frac{1}{2}$ yards run on the flat, or 40 to 80 inches of vertical work in the same time.

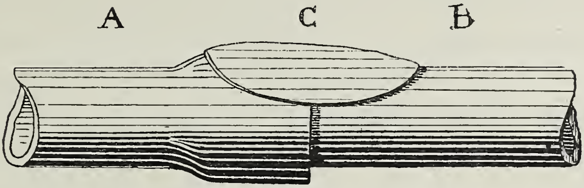


FIG. 173.—Jointing two horizontal pipes.

The soldering of the convex under side of a horizontal pipe is an almost impossible task for the blowpipe. Consequently, where the jointing of two horizontal or slightly inclined pipes (A, B, Fig. 173) is in question, they cannot be soldered all round from the outside; and in such event the one pipe (A) is slightly enlarged at the mouth so as to receive the end of the other pipe (B). A hole C is then made at the top, through which the blowpipe is introduced, and the soldering is effected on the inside

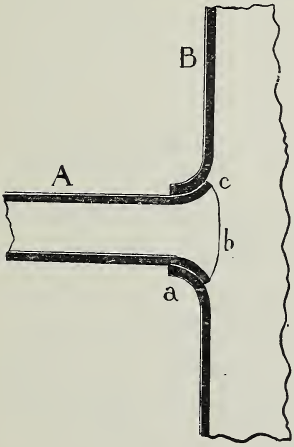


FIG. 174.—Fitting a leaden pipe to a vertical wall, accessible on the rear face.

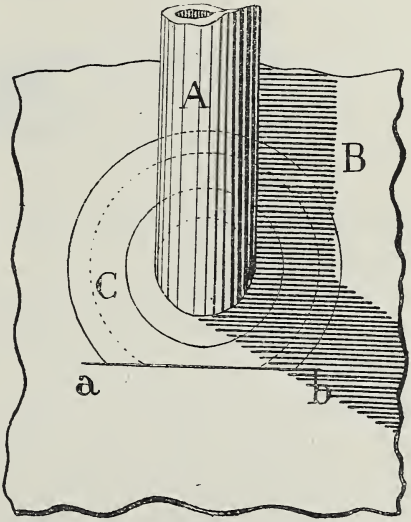


FIG. 175.—Fitting a leaden pipe to a vertical wall, inaccessible from the back.

of the pipe, which done, the hole C is covered with a leaden plate readily fastened on by soldering.

If it is desired to fasten a pipe A to a vertical sheet B (Figs. 174, 175), and access to the rear of the latter is possible, a circular hole, of rather smaller diameter than the pipe, is cut in the sheet. The metal round the hole is then turned up outwards so as to form a neck large enough to admit the pipe without too much play. The latter is next fixed in position in such a manner that the edge rests on the turned-up part at *a*, and the work of soldering is begun, the blowpipe attacking the edge of the pipe in order to form the ridge. This is continued as far as *b*, from which point onwards the sheet B is attacked until *c* is reached.

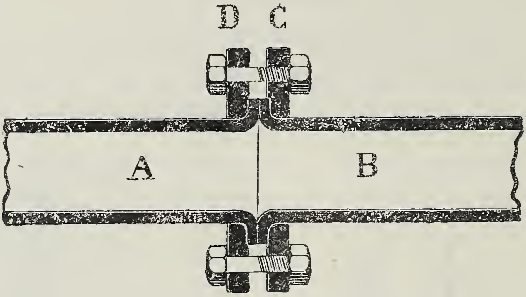


FIG. 176.—Bolted loose-flange joint for pipes.

When the wall cannot be got at from the back, or when it is desired to have the soldered joint on the same side as the pipe, the latter is first fitted with a collar C (Fig. 175). Then, in addition to the opening necessary for the reception of the pipe, a slit *a b* is cut in the wall, and, after the edge of the collar has been set in this slit, soldering is begun along the straight line *a b*, and continued upwards all round the collar.

Occasionally a bolted loose-flange joint is required for pipes. In this case the two adjacent ends of the pipes are flanged after the loose flanges have been slipped in position, and, the ends being put together, the loose flanges are fastened with bolts and nuts (Fig. 176), which squeeze the lead flanges together and make a perfectly tight joint.

112. **Possible Improvements in the Treatment of Pyritic**

Lignites.—The method of manufacture already described is costly, and, although under proper management it is still profitable, the small margin of profit left is sufficient justification for the endeavour to find more economical methods of procedure, apart from all other considerations.

The prospects of success in such endeavour have been considered by the author, and, in collaboration with A. Vivien of St. Quentin, he has made a special study of the preparation and lixiviation of the ore.

A. ENRICHMENT OF THE ORE.—When prepared in the ordinary manner the ore furnishes a poor raw material, expensive to handle, and varying in yield according to the weather. This poverty necessitates the accumulation of enormous stocks, which cannot possibly be protected in a satisfactory manner from the lixiviating action of rain, considerable losses being the result.

The high temperature generated during the oxidation process causes the formation of insoluble sub-salts, and therefore a portion of the sulphuric acid produced is left unutilised. Moreover, the work is slow, costly, unhealthy, and difficult to control.

An investigation of the sequence of operations during the oxidation process will readily show that the oxidation develops a considerable volume of heat. Even after a lapse of three months the temperature of the large heaps still remains about 100° C.; and the author has endeavoured to utilise this heat for attacking the excess clay in the mass, by means of sulphuric acid, without expense. The fear that the presence of organic matter in the mineral would lead to a loss of sulphur dioxide, resulting from the decomposition of part of the sulphuric acid, has been proved groundless by the result of these experiments.

The first trial was conducted as follows:—

A 45-ton heap of the mineral was treated with 52 cwt. of 60° Bé. sulphuric acid, which was left to react for about a fortnight, a similar heap adjoining being left without acid as a check. Samples were taken with great care, pulverised, and subjected to analysis, with the following results:—

(1) *Lixiviation of* 100 *grms. with* 500 *grms. water*—

	Acidified Cinder.	Check Cinder.
Moisture	15·65	10·80
Volume of liquor obtained	435 c.c.	425 c.c.
Sp. gr.	1·029	1·025
Corresponding degree Baumé	4°	3·4°
Weight of alum recovered, referred to 100 grms. of dry substance	15·47 grms.	8·76 grms.

(2) *Comparative Analysis of Cinder; results referred to dry matter*—

	Acidified Cinder.	Check Cinder.	Difference.
Ferrous sulphate ($FeSO_4$, $7H_2O$)	14·50	10·30	+4·20
Ferric ,, ($Fe_2(SO_4)_3$, $9H_2O$)	1·20	2·25	−1·05
Aluminium ,, ($Al_2(SO_4)_3$, $18H_2O$)	17·04	10·22	+6·82
Soluble sulphuric acid (H_2SO_4)	21·52	15·78	+5·74

The quantity of acid used was 4·260 kilos. per cubic metre, and therefore more was recovered than the amount initially present.

This first test showed that the attack proceeds fairly rapidly and without loss; but, owing to the great difficulty experienced in sampling, it was felt desirable to repeat under conditions of greater accuracy. Again, a difficulty having arisen in distributing the acids to the small heaps in a practical manner, it was thought advisable to wait until the large-heap stage before adding the acid. In order to ensure identicity of conditions, the work was performed as follows:—

A certain quantity of the oxidised lignites was taken at the time of making the large heaps, and sifted to render it homogeneous. An accurately weighed amount of this sample was then placed in boxes and treated with a known quantity of sulphuric acid; and, after the addition of a little water, the closed boxes were re-weighed and placed in the heap in course of building, a note being taken of the weights in each case. When the attack was deemed to have sufficiently progressed the boxes were taken out of the heaps and weighed again, the difference in weight noted; and, the contents having been reduced to powder, the samples for analysis were taken.

A preliminary test carried out on this plan gave the following results:—

No. of Test.	Weight of Substance.	Weight of 60° B. Sulphuric Acid taken.	Weight of Water added.	Weight before the experiment.	Weight after the experiment.
	kilos.	kilos.	kilos.	kilos.	kilos.
1	50	5	1	56	56
2	50	10	3	63	65
3 (check)	50	nil	nil	50	50

Temperature on opening the boxes, 90° C.
Duration of experiment, 20 days.
N.B.—No. 2 sample, having been placed in a damp part of the heap, had absorbed water.

Substances estimated; referred to the weights found after experiment.	Test 1. 10 per cent. of 60° Bé. acid.	Test 2. 20 per cent. of 60° Bé. acid.	Test 3. Check.
Insoluble matter	64·62	61·67	67·80
Ferrous sulphate ($FeSO_4$, $7H_2O$) (*from the total iron*)	28·47	30·16	21·89
Aluminium sulphate ($Al_2(SO_4)_3$) . .	10·49	18·77	4·35
Sulphuric acid (H_2SO_4) . . .	19·32	31·82	13·86
Alum corresponding to the alumina .	27·83	49·77	11·56

The second trial, performed under identical conditions, came out as follows:—

No. of Sample.	Weight of Substance.	Weight of 60° Bé. Sulphuric Acid taken.	Weight of Water added.
	kilos.	kilos.	kilos.
1	10	1·0	0·4
2	10	1·5	0·6
3	10	2·0	0·8
4	10	1·0*	0·6
5 (check)	10	nil	nil

* Sludge acid from petroleum refining, containing 850 grms. H_2SO_4 per litre.

The time occupied in this case was ten weeks, and the temperature of the material at the time of opening the boxes = 100° C.

From these experiments it follows that the added sulphuric acid attaches itself mainly to the alumina; that it is completely utilised; and that a larger quantity is recovered than was added in the first place,—a result evidently due to the sub-salts having been rendered soluble.

Substances estimated; referred to the weights found after the experiment.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
	kilos.	kilos.	kilos.	kilos.	kilos.
Total iron	7·28	7·91	8·37	7·57	5·15
Corresponding to crystallised ferrous sulphate ($FeSO_4$, $7H_2O$) . .	34·70	39·26	39·90	36·07	25·56
Alumina	1·83	2·39	3·43	1·76	0·41
Corresponding to crystallised aluminium sulphate ($Al_2(SO_4)_3$, $18H_2O$) .	11·81	15·48	18·94	11·43	2·65
Or alum	16·25	21·23	30·45	15·63	3·44
Total sulphuric acid (H_2SO_4) . .	22·65	24·70	30·56	23·07	14·21
Of which, uncombined with iron or alumina	4·70*	6·03†	7·52‡	4·97‖	4·10

* 4·13 per cent. † 4·75 per cent. ‡ 5·34 per cent. ‖ 4·11 per cent.

It would therefore seem advantageous to treat the ore in this fashion; the more so because the earliest consequence of the considerable enrichment of the material is to appreciably diminish the cost of labour, consumption of coal, waste, etc.

B. LIXIVIATION.—I. *Theory of Systematic Lixiviation.*—In studying this stage of the process it is highly necessary to be able to follow up all the phases by calculation. We will therefore, in the first place, trace out the simple relations connecting the different quantities—such as volume of liquid to be drawn off, weight of material lixiviated, density of the liquors, etc.—coming into play in the process of lixiviation.

Let us take a battery of apparatus composed of a series of units, 1, 2, 3 . . . $m-1$, m, in which the direction of circulation is from 1 towards m; and assume that the liquor stays long enough in each unit for the concentration to be identical throughout the series.

A constant volume v of liquor is retained by the insoluble matters.

Then, let

V_t be the volume of liquor to be drawn off;

V_o, the volume of water fed to the battery for each operation, and consequently the volume of liquor passing from one unit to another;

P, the weight of material placed in the last unit;

π, the weight of soluble matter in P;

$\pi_1, \pi_2, \ldots \pi_n, \pi_{n+1}$, the weight of soluble matter per unit of volume in the intermediate or final liquors;

$1 + d_1,\ 1 + d_2, \ldots 1 + d_n,\ 1 + d_{n+1}$, the densities of these liquors.

The liquids and solids are introduced in an invariable, though intermittent, manner, and the tendency is towards the establishment of a permanent *régime.* Let us suppose this to be accomplished, and the apparatus in work.

Take three units in series, $n - 1$, n, $n + 1$; then $n + 1$ becomes n, losing one step, on the addition to the series of a freshly charged unit forming the final member.

This unit n, previously $n + 1$, contains the residues and the liquor impregnating same, representing an amount of soluble salts corresponding to

$$v \times \pi_{n+1}.$$

On the other hand, the new unit n receives from its immediate predecessor a volume V_o of liquor, representing a quantity of salts equivalent to

$$V_o \times \pi_{n-1}.$$

Consequently, at a given moment n contains a weight of soluble salts equal to

$$v \times \pi_{n+1} + V_o \times \pi_{n-1}.$$

In the next turn, however, n becomes $n - 1$, $n + 1$ becomes n, and so on; the unit n loses a quantity of soluble salts represented by the amount of water impregnating the residues, *i.e.* $v \times \pi_n$, plus that contained in the liquor passing into the unit $n + 1$, *i.e.* $V_o\pi_n$, or in all

$$v \times \pi_n + V_o \times \pi_n.$$

The weight of soluble salts entering this unit is evidently the same as the amount leaving it, and is equivalent to

$$v \times \pi_{n+1} + V_o\pi_{n-1} = v \times \pi_n + V_o \times \pi_n.$$

Or

$$v(\pi_{n+1} - \pi_n) = V_o(\pi_n - \pi_{n-1})$$

$$\pi_{n+1} - \pi_n = \frac{V_o}{v}(\pi_n - \pi_{n-1}).$$

If we apply this relation to all the vats or units, and make in succession $n = 1, 2, 3, \ldots m$, we shall then have

$$\left.\begin{array}{ll}\text{Unit } 1 \ldots\ldots & \pi_2 - \pi_1 = \frac{V_o}{v} \times \pi_1 \\ \text{Unit } 2 \ldots\ldots & \pi_3 - \pi_2 = \frac{V_o}{v}(\pi_2 - \pi_1) \\ \ldots\ldots & \ldots\ldots \\ \ldots\ldots & \ldots\ldots \\ \text{Unit } m - 1 \ldots & \pi_m - \pi_{m-1} = \frac{V_o}{v}(\pi_{m-1} - \pi_{m-2}) \end{array}\right\} \text{(A)}$$

On multiplying these equations one upon the other we have

$$(\pi_2 - \pi_1)(\pi_3 - \pi_2) \ldots (\pi_m - \pi_{m-1}) = \left(\frac{V_o}{v}\pi_1\right)\left[\frac{V_o}{v}(\pi_2 - \pi_1)\right] \ldots$$

$$\ldots \left[\frac{V_o}{v}(\pi_{m-2} - \pi_{m-2})\right]$$

$$= \left(\frac{V_o}{v}\right)^{m-1}\left[\pi_1(\pi_2 - \pi_1) \ldots (\pi_{m-1} - \pi_{m-2})\right]$$

and on dividing by

$$(\pi_2 - \pi_1)(\pi_3 - \pi_2) \ldots (\pi_{m-1} - \pi_{m-2})$$

obtain

$$\pi_m - \pi_{m-1} = \left(\frac{V_o}{v}\right)^{m-1} \times \pi_1 \qquad (1)$$

If we now add together the equations A we obtain

$$(\pi_2 - \pi_1) + (\pi_3 - \pi_2) + \ldots + (\pi_m - \pi_{m-1}) = \frac{V_o}{v}\pi_1 + \frac{V_o}{v}(\pi_2 - \pi_1) +$$

$$\ldots + \frac{V^o}{v}(\pi_{m-1} - \pi_{m-2})$$

Or

$$\pi_m - \pi_1 = \frac{V_o}{v}(\pi_{m-1}) \qquad (2)$$

from which can be deduced

$$\pi_{m-1} = \frac{\pi_m - \pi_1}{\frac{V_o}{v}} \qquad (3)$$

Let us substitute this value of π_{m-1} in equation (1)—

$$\pi_m - \frac{\pi_m - \pi_1}{\frac{V_o}{v}} = \left(\frac{V_o}{v}\right)^{m-1} \times \pi_1$$

whence

$$\frac{V_o}{v} \times \pi_m - \pi_m + \pi_1 = \left(\frac{V_o}{v}\right)^{m-1} \times \pi_1$$

$$\pi_m\left(\frac{V_o}{v} - 1\right) = \left(\frac{V_o}{v}\right) \times \pi_1 - \pi_1$$

$$= \pi_1\left[\left(\frac{V^o}{v}\right)^m - 1\right]$$

and hence

$$\pi_m = \frac{\pi_1\left[\left(\frac{V_o}{v}\right)^m - 1\right]}{\frac{V_o}{v} - 1}$$

$$\pi_m = \frac{\left(\frac{V_o}{v}\right)^m - 1}{\frac{V_o}{v} - 1} \times \pi_1 \qquad \text{(B)}$$

From this can be deduced

$$\left(\frac{V_o}{v}\right)^m - 1 = \frac{\pi^m}{\pi_1}\left(\frac{V_o}{v} - 1\right)$$

$$\left(\frac{V_o}{v}\right)^m = \frac{\pi_m}{\pi_1}\left(\frac{V_o}{v} - 1\right) + 1 = \frac{\pi^m\left(\frac{V_o}{v} - 1\right) + \pi_1}{\pi_1} \ . \ . \ . \qquad (4)$$

If we apply the primordial formula to the m vat, we have

$$\pi + V_o(\pi_{m-1}) = v \times \pi_m + V_t \times \pi_m,$$

and, by applying the value already found for π_{m-1},

$$\pi + V_o \frac{\pi_m - \pi_1}{\frac{V_o}{v}} = v \times \pi_m + V_t \times \pi_m$$

$$\pi + \frac{V_o \times \pi_m - V_o \times \pi_1}{\frac{V_o}{v}} = v \times \pi_m + V_t \times \pi_m = \pi_m(v + V_t)$$

$$\pi\left(\frac{V_o}{v}\right) + V_o \times \pi_m - V_o \times \pi_1 = \pi_m(v + V_t)\frac{V_o}{v}$$

$$V_o \times \pi_m - V_o \times \pi_1 = (v \times \pi_m + V_t\pi_m)\frac{V_o}{v} - \pi\frac{V_o}{v}$$

$$= \frac{V_o}{v}v\pi_m + \frac{V_o}{v}V_t\pi_m - \frac{V_o}{v}\pi$$

$$= \frac{V_o v\pi_m + V_o V_t\pi_m - V_o\pi}{v}$$

$$\begin{aligned} vV_o\pi_m - vV_o\pi_1 &= V_o v\pi_m + V_o V_t\pi_m - V_o\pi \\ v\pi_m - v\pi_1 &= v\pi_m + V_t\pi_m - \pi \\ \pi + v\pi_m - v\pi_1 &= v\pi_m + V_t\pi_m \\ \pi &= V_t\pi_m + v\pi_1 \qquad \text{(C)} \end{aligned}$$

Let us assume that the water throughout the system is constant. The volume entering is V_o: therefore an equal volume of water should leave the series—

$$\begin{aligned} V_o &= v(1 + d_1) - v\pi_1 + V_t(1 + d_m) - V_t\pi_m \\ V_o &= v(1 + d_1 - \pi_1) + V_t(1 + d_m - \pi_m) \qquad \text{(D)} \end{aligned}$$

To sum up, we obtain three ratios between the values π, v, V_o, V_t, π_m, π_1, d_1, d_m, and m. These values are for the most part arbitrary, and dependent on the requirements of the manufacturing process: thus $\frac{d_m}{d_1} = \frac{\pi_m}{\pi_1}$; π is known; v can be determined by experiment; $1 + d_m$, the density of the final liquor, will vary according to the conditions of manufacture and the result in view; π_m is known; $1 + d$, or π, is the result of the final washing; and P (from whence comes the values π and v) is a fixed quantity; so that there only remain to be determined V_o, V_t, and m.

$$V_o = v(1 + d_1 - \pi_1) + V_t(1 + d_m - \pi_m) \quad . \quad . \qquad (1)$$

$$\pi = V_t\pi_m + v\pi_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

$$\left(\frac{V^o}{v}\right)^m = \frac{\left(\frac{V^o}{v} - 1\right) + \pi_1}{\pi_1} - \pi_m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

These three ratios comprise all the factors of systematic lixiviation, and enable all the problems of this operation to be solved.

II. *Hot Extraction.*—The usual method of extraction is attended with numerous inconveniences in practice, since the liquors obtained are very dilute and have to be concentrated, which entails considerable consumption of fuel, much labour, etc. In consequence of the large area of the apparatus the extraction is often defective, tedious, and does not properly exhaust the mineral, especially in winter.

The work is very troublesome, and considerable loss by infiltration occurs in consequence of the leaks formed in the masonry.

The author has had the idea of a process of extraction in closed vessels under pressure, with small charges, and at a temperature of 100°. In fact, the mineral to be treated consists essentially of an insoluble porous skeleton, containing a mixture of soluble salts, for whose solution a temperature of 100° is the best. It is *à priori* evident that by causing hot liquor to circulate through this mineral a sufficient number of times a hot saturated solution will be formed, *i.e.* one that does not require concentration. If it proves that this result can be obtained with a smaller expenditure of fuel than the concentration process, the advantage of the new system will be evident. In the ordinary method the liquor measures 28° Bé. only, and must be concentrated by evaporation to 42° Bé., *i.e.* by applying the formula

$$V = 1000 \frac{d^1 - d}{d^1 - 1}.$$

About 420 litres of water must be removed per cubic metre of liquor. The amount of heat theoretically necessary for this evaporation—taking the specific heat of the liquid as unity—is given by the formula $Q = P\ (606{\cdot}5 + 0{\cdot}305 \times t - \theta)$, that is to say, in the present case about 250,000 calories. To these calories must be added the heat required for raising the residual volume to 100°, *i.e.* 49,000 cal., assuming the initial temperature to be 15°, or a total quantity of heat represented by 306,000 cals.

By the hot-extraction method the consumption of heat is represented merely by the number of calories necessary to raise the temperature of the concentrated liquor from 15° to 100°, *i.e.* 49,000 cals., since this volume of liquor will be equal to that furnished by the evaporation process. That is to say, we have in round numbers a saving of 250,000 cals. per cubic metre of 28° Bé. liquor, or per each 500 metres of concentrated liquor; *i.e.* a little more than $\frac{5}{6}$ of the total quantity. The advantage is therefore more than appreciable. As regards the means of performing this operation, the first idea that presents itself is that of an apparatus similar to that of the diffusion batteries used in sugar works. This apparatus can be pictured as lined with thin sheet-lead, and somewhat flat in shape, provided with a filtering surface of asbestos cloth or glass wool, leaden conduits, etc. The water would be turned on, but, in order to avoid loss of heat in the spent mineral, only the last members of the series would be heated, and that, too, after the liquor was already in a state of cold saturation. In this manner the heat stored up in the spent mineral would be recovered by the subsequent cold liquid, and each unit would not be emptied until thoroughly cooled down. At this moment, *i.e.* when the cold saturation had been effected, the residual liquors from the alum process could be introduced, thus effecting an economy of fresh water. From the trials made by the author the thickness of the charge should not exceed 20 to 24 inches in each unit, in order to prevent undue resistance to the passage of the liquor. Perhaps, however, by arranging more favourable conditions this thickness can be increased, and would correspond to an increase in the volume of liquid obtained.

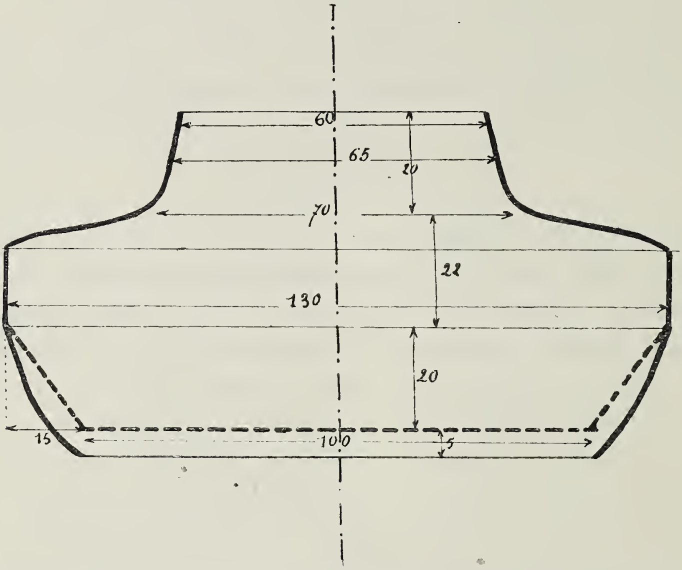


FIG. 177.—Hot extraction. Diagram of a unit of an extraction battery.

The number of units in the battery would be easily calculable for each particular case by means of the formulæ already given, and would always be small; consequently the cost of the installation would not be very high.

The concentrated hot liquors would be caught in a reservoir fitted with baffles, where the insoluble matters would settle down;

from those they would pass to the reduction process (which of course would be effected in the warm), and finally to the crystallisers.

Other improvements are also possible in the treatment of lignites; such, for example, as the filtration of the saturated alum liquors before casting the blocks, which treatment, by removing the insoluble matters usually present, would increase the quantity of merchantable alum produced. For this purpose a filter, of the Philippe type, employed for filtering syrups in sugar works, but fitted with heating apparatus to prevent a crystallisation of a concentrated alum solution, might be used.

It is evident that in this case it would no longer be possible to lute the bottom joint of the mould with clay, but that in order to ensure proper working this joint would have to be made of caoutchouc, or some other suitable material.

Another improvement that may be introduced applies to the manufacture of purified alum direct in crystallising the crude alum by agitation, in order to secure the deposition of very small crystals. This mass of crystals, when drawn in the hydro-extractor, clarified, macerated with alum water, drawn off, and clarified anew, furnishes an alum which, the author is satisfied, will give purified alum after a single re-crystallisation.

Concerning the crystallisation process generally, both for ferrous sulphate and alum, it is evident that the crystallisers set in the ground are very defective. Wooden crystallisers, lined inside with thin sheet-lead, and raised above the ground, such as those described in dealing with the treatment of alunite, would be much more practical. In addition to the fact that on demolishing the crystallisers the old lead retains its value, and that consequently an installation of this kind, although costly, always represents a portion of the capital expenditure, with this system leaks can be easily detected and repaired, and a considerable saving of labour is effected. In fact, the mother liquor can be drained off by a single process of syphoning, which saves the expense of pumping—a serious matter in view of the enormous volume of liquor. Furthermore, the crystallisers can be arranged to serve as washers, thus avoiding a double handling of the salt.

So as not to go beyond our subject, which is chiefly concerned with describing the industries forming the object of the present work, we will not further enlarge on this point, but will now pass to the manufacture of ferric sulphate.

§ 3. MANUFACTURE OF ORDINARY FERRIC SULPHATE.

113. **Introduction.**—Until within the last few years ferric sulphate was generally looked upon as a mere laboratory product, or, at any rate, was only manufactured in small quantities industrially. Nevertheless, it has long been known that this salt, already used in dyeing,* was useful for purposes of sanitation, by reason of its property of combining with organic matters and preventing their putrefaction. Among the numerous patented processes for manufacturing ferric sulphate we need only mention those of Marguerite and Rohart, which are now of merely historic interest; and, above all, the elegant and practical method invented by Buisine, the distinguished professor of science at Lille and the Institut Industriel du Nord.

114. **The Marguerite Process.**—This process was devised for manufacturing ferric sulphate from oxide minerals, pyritic cinder, etc., which substances, under ordinary conditions, are difficult to attack with sulphuric acid.

The *modus operandi* claimed by the inventor consists in treating oxide of iron by sulphuric acid, in presence of a small quantity of hydrochloric acid, which facilitates the reaction. The hydrochloric acid, which acts the more energetically, forms at first ferric chloride, according to the equation

$$Fe_2O_3 + 6HCl = Fe_2Cl_6 + 3H_2O.$$

This ferric chloride is produced in presence of an excess of sulphuric acid, which acts upon it in turn—

$$Fe_2Cl_6 + 3H_2SO_4 = Fe_2(SO_4)_3 + 6HCl.$$

The small quantity of hydrochloric acid is thus constantly re-

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* Ferric sulphate was employed in dyeing, in consequence of the researches of Raymond, *i.e.* early in the nineteenth century. It was first used for blue, and for this purpose was prepared from ferrous sulphate by moderate calcination.

generated, and the cycle of operations continues as long as there is any ferric oxide and excess of sulphuric acid remaining.

115. **The Rohart Process.**—Although the inventor of this process, Rohart's principal aim in connection with ferric sulphate was to investigate its disinfectant properties, and it was only subsequent to the date of his patent (1882) that the importance of this application of the salt in question began to be properly appreciated.

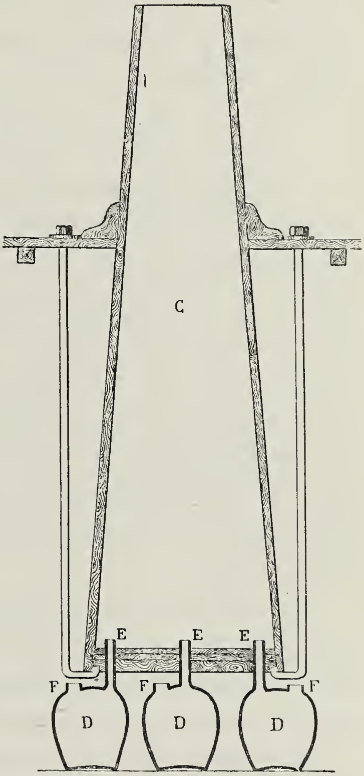

Fig. 178.—Manufacture of ferric sulphate (Rohart process).

The Rohart process is based on the conversion of ferrous sulphate into ferric sulphate, under the influence of nitric acid in presence of the necessary amount of sulphuric acid. The apparatus for this purpose consisted of a wooden trunco-conical vessel C (Fig. 178) suspended over a group of five glass carboys D D, the necks of which, E E, projected through the bottom of C.

To obtain ferric sulphate with this apparatus, 36° Bé. nitric acid was first poured into the carboys. Meanwhile a mixture was prepared by heating and stirring suitable proportions of sulphuric acid, ferrous sulphate, and water in a cast-iron pan; this mixture being poured into the vessel C as soon as it had become homogeneous, and without waiting for it to cool. The sediment left in the pan was afterwards broken up and filled into the flasks D through the necks F.

The reaction commenced at once, and proceeded unaided. To decrease the considerable consumption of nitric acid entailed by the method, the inventor, in his specification, recommends injections of air into the carboys.

The resulting ferric sulphate was acid, and had to be neutralised with sodium carbonate or ferric hydrate.

116. **Ordinary Peroxidation Process with Regeneration of the Nitrous Products.**—This process will be described later on in dealing with the basic ferric sulphate known as Rouil mordant, in the manufacture of which it is still employed.

117. **The Buisine Process.**—This method consists in attacking roasted iron pyrites with sulphuric acid. The very simple reaction is represented by the equation

$$3H_2SO_4 + Fe_2O_3 = Fe_2(SO_4)_3 + 3H_2O.$$

Iron pyrites, the actual raw material employed, furnishes the two products necessary in this method of preparing ferric sulphate, namely, iron peroxide and sulphuric acid, the sulphur dioxide formed by roasting the pyrites being converted into sulphuric acid in leaden chambers. The method is therefore specially adapted for use in large chemical works possessed of the necessary plant, and producing, on the one hand, roasted pyrites, and, on the other, 60° Bé. sulphuric acid; in fact, the reaction goes on most actively with this strength of acid, and at a temperature of 120° C.—that at which the acid leaves the Glover tower.

The operation is extremely simple. The hot acid is run direct from the Glover tower into a cast-iron pan, heated from below, which pan is then charged with roasted pyrites, in powder, as it leaves the furnace, but cooled and sifted if necessary.

On stirring the mass the reaction commences, and is stimulated and carried to completion by the aid of heat, the temperature being raised to 250° to 300° C. Steam alone is liberated, and the iron oxide is almost entirely consumed, the product generally containing not more than 5 per cent. of insoluble residue. The ferric sulphate forms 75 to 95 per cent. of the total.

In practice, 45 to 50 parts of roasted pyrites are taken for every 100 parts of acid, according to the composition desired for the product, which may be either normal ferric sulphate or ferric sulphate containing a larger or smaller excess of free sulphuric acid. This has its advantages, because in certain cases the treatment of waste liquors may require a neutral ferric sulphate or one of known acidity, according to circumstances. The temperature of the reaction also affects the composition of the product, as is shown by the following table compiled by Buisine:—

Constituents.	Temperature of Reaction.		
	130°	180°	300° C.
Water	20·63	8·41	0 per cent.
Insoluble Fe_2O_3	11·75	7·38	2·74 ,,
Soluble Fe_2O_3	18·89	29·93	40·29 ,,
Total H_2SO_4	55·10	64·38	70·93 ,,
Free H_2SO_4	20·39	9·39	...
Normal ferric sulphate	47·23	74·82	96·65 ,,

The following analytical values of another ferric sulphate prepared by the Buisine process were obtained by M. Vivien of St. Quentin:—

Ferric sulphate	60·00
Free sulphuric acid	9·49
Ferric oxide	11·40
Ferrous sulphide	0·56
Sand	2·04
Volatile matter	1·16
Moisture	11·64
Sundries and undetermined	3·71
Total	100·00

The Buisine sulphate is a greyish dry powder, easy to pack and transport. It is anhydrous, and in that condition is very sparingly soluble in water, but after hydration—which occurs gradually in the cold, though more rapidly in the warm—it becomes exceedingly soluble.

When mixed with 15 to 20 per cent. of water, ferric sulphate sets slowly, like gypsum. As we shall see later on, this property has been utilised for the production of ferric sulphate briquettes, a very suitable form of this salt for many uses. Briquettes have also been made containing phenols and other antiseptics for use in certain special cases (see Part III., USES).

§ 4. MANUFACTURE OF BASIC FERRIC SULPHATE, OR ROUIL MORDANT *

118. **Introduction.**—The preparations known by the name of Rouil mordant consist mainly of concentrated solutions of a basic ferric salt, largely used in dyeing, especially for silks. They form the object of an important industry, mainly located at Lyons, which at the same time is the principal centre of consumption of the products.

This industry was founded by Raymond, and the first manufactory was started at Lyons early in the nineteenth century; it was still in existence at about 1830.

In 1876 the daily output of the Lyons factories was 25 to 30 tons of this product. The amount now produced is difficult to estimate, considerable quantities being made in Rouen, Amiens, Paris, Lille, Chailvet, etc., as well as at Lyons.

The preparation most used in dyeing is that known as rouil sulphate. When first Raymond, who was professor of chemistry at Lyons, proposed to use ferric sulphate for producing blue with potassium cyanide, the salt employed was prepared by calcining ferrous sulphate; but subsequently, when working on a manufacturing scale, he modified the process and employed nitric acid for peroxidising the ferrous sulphate. At first the operation was conducted, without any attempt at recovering the nitrous products, by mixing nitric acid, sulphuric acid, and ferrous sulphate together in casks. The resulting product was costly, and necessarily imperfect, and it was only at a later date that the idea arose of working in vats, and recovering the nitrous products.

A. Rouil Sulphate.—This preparation is, in the liquid form, dark reddish brown by reflected light, rusty by transmitted light, and contains in solution a ferric salt, which should preferably approximate in composition to the formula $(Fe_2)_2(SO_4)_5$. The liquid should measure 40° to 46° Bé.

At one time two kinds of this sulphate were prepared—that for blacks (*Rouil pour noirs*) containing an excess of ferrous sulphate, whilst that for blues (*Rouil pour bleus*) was completely

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* According to Littré, this word rouil is a corruption of *rouille* = rust.

peroxidised. This distinction has now been abolished, and endeavours are confined to producing a mordant containing a minimum of ferrous sulphate.

Other classes of *rouil* are known; but being of limited employment need only brief mention here.

B. ROUIL NITRATE.—Deep red liquor, generally home-made by the dyer, by gradually adding scrap-iron to nitric acid until an ochreous deposit of ferric sub-nitrate is formed.

C. ROUIL ACETATE.—This is also a dark red-brown liquor of 20° Bé. density, and is prepared by the double decomposition of ordinary *rouil* and lead acetate.

D. ROUIL CHLORIDE.—A reddish-yellow liquor. Despite numerous trials, this variety has always been abandoned on account of the difficulty with which it forms insoluble sub-salts on contact with water, the production of which salts is a characteristic property of the other rouil preparations, and one *inter alia* that justifies their employment in silk dyeing.

E. ROUIL ACETO-NITRATE.—This is dark red in colour. It is prepared in the same manner as rouil nitrate, except that the addition of scrap-iron is continued until the whole mass sets firm. The mass of sub-salt is then treated in enamelled cast-iron pans with hot acetic acid, the sub-salt being kept in excess throughout.

Except this last one, these different *rouils* present little of interest.

119. **Rouil Sulphate — Manufacture.** — *A.* NITRIC ACID METHOD.—This, the process in general use hitherto, consists in oxidising commercial ferrous sulphate with nitric acid in presence of a certain proportion of sulphuric acid, and is based on the following reaction, which represents the production of normal ferric sulphate—

$$6[FeSO_4, 7H_2O] + 3H_2SO_4 + 2HNO_3$$
$$= 3[Fe_2(SO_4)_3, 9H_2O] + 2NO + 19H_2O.$$

The process appears exceedingly simple, but, as we shall see later, is in reality difficult, and entails skilled labour.

(1) *Plant.*—This is simple, and comprises a peroxidation vat, a recuperator for the nitrous products, and storage vats for the *rouil.*

The peroxidiser is of lead or cast-iron, the former being preferable on the score of economy, since it is more durable, easily repaired by the hydrogen blowpipe; and when the vats are pulled down the old metal is worth a good deal of its original price. The vat is fitted at the bottom with a discharge pipe which is closed by a wooden plug. The lead used is $\frac{2}{5}$ to $\frac{1}{2}$ inch thick. Towards the upper edge the vat widens out suddenly, so as to be able to cope with the effervescence produced in the mass by the violence of the reaction.

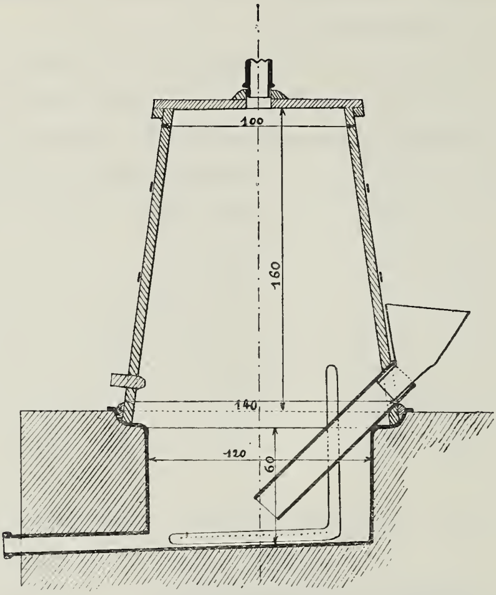

FIG. 179.—Rouil mordant process. Peroxidation vat.

On this widened part rests a wooden cone, surmounted by a pipe for the escape of the gases, and also pierced by three openings—one, generally closed, for inserting a stirring rod; the second and smaller one admitting the steam pipe, which terminates below in a coil; whilst the third and largest opening is traversed by an earthenware pipe extending to within 4 to 6 inches of the bottom of the vat. Into the mouth of this pipe fits a leaden funnel for introducing the charge. All the joints are luted with brick earth.

The gas-escape pipe leads to a series of condensers for the removal of moisture, the gas then passing into a battery of divided carboys and thence through a set of three coke scrubbers into a chimney shaft of good draught. The joints are luted with a mixture of $\frac{1}{3}$ Portland cement and $\frac{2}{3}$ brick earth with sufficient melted pitch to make a plastic paste. The mixture must be used whilst fresh, as it will not keep.

The installation is completed by a series of lead-lined wooden reservoirs placed over against the peroxidising vat, and destined to store the liquid product.

(2) *Manufacturing Process.*—The vat shown in Fig. 179 furnishes about 12 cwt. of merchantable product at each charge. It is charged with about $4\frac{1}{2}$ gallons of water, or saturated solution of iron sulphate, followed by $2\frac{1}{2}$ gallons of 60° Bé. sulphuric acid and $3\frac{1}{4}$ gallons of 36° Bé. nitric acid. Steam is then turned on, and, when the contents are hot, commercial ferrous sulphate, in the state of small crystals, is shovelled in, a little at a time. Each shovelful produces strong effervescence owing to the abundant liberation of nitrogen dioxide, a small portion of which escapes as red fumes through the charging pipe, and enables the progress of the reaction to be followed. When the reaction slackens, 9 to 12 gallons of weak (20° to 22° Bé.) nitric acid from the recuperation plant are run in, followed by a further addition of ferrous sulphate. When the red fumes cease to escape through the charging pipe, and no particular effervescence can be heard on the addition of more ferrous sulphate, the peroxidation is complete. Steam is then turned on full, so as to superheat the mass and cause the *rouil* to assume its characteristic colour, after which the liquid is run off into the storage reservoirs.

At the end of several days the liquor deposits an abundant sediment of insoluble sub-salts, which constitute a considerable amount of waste.

Fire heat may be used instead of steam, but is not to be recommended. In this case the vat is first charged with about 30 gallons of water instead of $4\frac{1}{2}$ gallons. As the final weight of product is unchanged, 242 lbs. of steam, corresponding to $35\frac{1}{2}$ lbs. of coal, are consumed in the steam-heating process, *i.e.* the cost per ton of product—taking the coal at 20s. per ton at the works—is under sevenpence. With fire heat about 80 lbs. of coal are required, which works out at the rate of 1s. 2d. per ton of product, the saving by using steam heat being therefore 8d. per ton; to say nothing of the reduction in the quantity of waste sub-salts produced in the final superheating stage, the greater ease in working and controlling the operation, and the diminished wear and tear of the vat.

(3) *Recuperating the Nitrous Products.*—Throughout the operation large volumes of nitric oxide are liberated, which by reason of the chimney draught are conveyed into the battery of carboys already mentioned. So far from being hermetically closed, the stoppers of some of these vessels are pierced with holes to facilitate admission of air, so that the nitric oxide, in passing through the vessels, becomes mixed with an increasing quantity of air, and is converted into nitrogen peroxide.

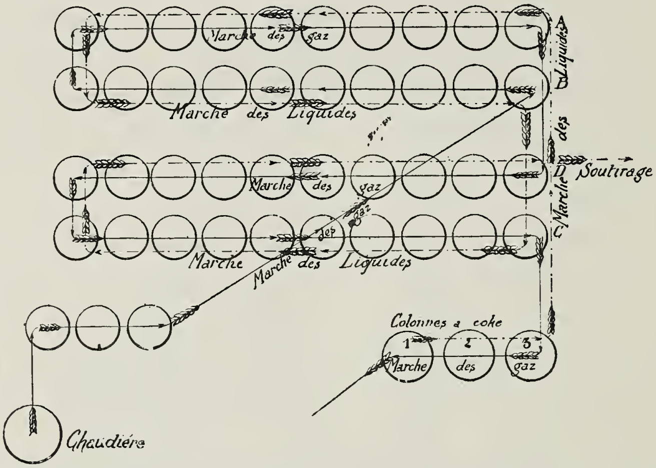

Fig. 180.—Manufacture of rouil mordant. Recuperation of the nitrous products.

Marche des gaz = course taken by the gas; Marche des liquides = course taken by the liquors; Chaudiére = peroxidation vat; Colonnes à coke = coke scrubbers; Soutirage = outflow.

On the other hand, the first of the coke scrubbers is charged with fresh water, the second receives the (0·5° to 1° Bé.) liquor from the first, and the third receives the 6° to 8° Bé. liquor from the second, and in turn discharges a 10° to 14° Bé. liquor, which is returned to the first carboy A of the battery; whilst the acid is drawn off from one of the carboys of the middle set B, which receives the gaseous products from the peroxidation vat. This acid has the density 16° to 18° Bé., and in turn is delivered into the third series of carboys C, the weak (20° to 22° Bé.) acid to be returned to the vat being drawn from the middle row of carboys D, which receives the gas from the first carboy A. The course taken by the gas and liquors is sketched in Fig. 180.

The nitrogen peroxide being in continual contact with water, the regeneration of the nitric acid proceeds according to the equations

$$N_2O_2 + O_2 = 2NO_2$$

$$6NO_2 + 2H_2O = 4HNO_3 + N_2O_2, \text{ etc.}$$

Theoretically, the whole of the nitric acid should be recovered in the weak liquor; but in practice a considerable loss occurs through leakage, secondary reactions, and the solution of a fraction of the nitric oxide in the liquors, in consequence of which it escapes oxidation.

Theory indicates that to peroxidise 75 parts of ferrous sulphate (equivalent to 100 parts of *rouil*) requires 5·70 parts of nitric acid, which should be recovered in the waste liquors. As a matter of fact, only about 4 parts of 36° Bé. acid, equal to 2·10 of pure acid, are recovered, the loss being therefore 36·8 per cent. of the initial acid introduced.

On tracing the course of the gases, it will be found that they consist of about $\frac{2}{3}$ nitric oxide on entering the battery, but merely traces of this oxide on their exit to the chimney stack.

The liquors collected in B are of a greenish colour, and are highly charged with nitric oxide. If stirred, numerous bubbles of gas are disengaged, and make their escape as red fumes.

This percentage decreases rapidly in the other vessels, whilst the amount of HNO_3 continually increases under the influence of progressive aëration.

This explains why the liquid has to be drawn off at the centre of the battery instead of at the same end as the gases, as would appear more rational. Another reason for the change is that the gases carry over a large quantity of water vapour, and, though the greater part of this is recovered on the way, a considerable proportion condenses in the first carboys of the battery, and thus dilutes the acid liquor there.

Even when air is blown into the battery by a Körting injector, to establish a regular circulation of the gases and liquor, the degree of acidity is always greater at the middle of the battery than in the end units.

This experiment was made with a view to ensuring more complete condensation and a consequent increase in density of the recovered acid. The results were very insignificant, the increase being only 1° to 2° Bé.

To ensure favourable recuperation and reduce the losses to a minimum, there must be no back pressure in the battery. This necessitates large outflow pipes and regularity of the reaction in the vat. If the temperature gets too high, or the ferrous sulphate is thrown in too quickly, there will be a sudden and enormous liberation of gas, which results in an increased pressure, loss of nitric oxide, momentary obstruction of the air supply, etc.

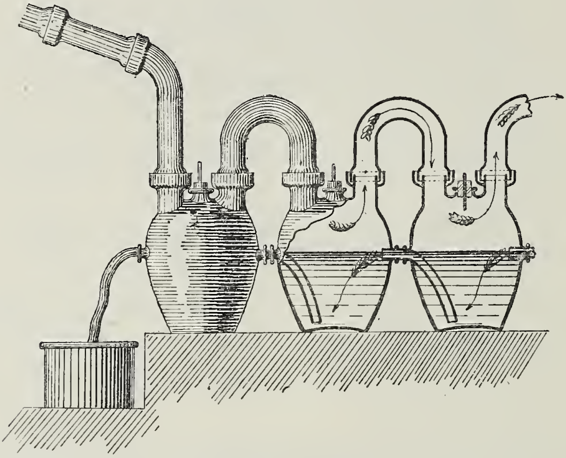

FIG. 181.—Manufacture of rouil mordant. Recuperation carboys.

If the ferrous sulphate be added too quickly when the vat is too cold another accident may arise, *i.e.* the fixation of the nitric oxide by the excess of ferrous sulphate, and the production of a brownish-black compound, which is difficult to decompose even by prolonged boiling: when this decomposition is effected it occurs suddenly with great violence, and forces part of the charge out of the vat. Hence it is necessary that the reaction should be looked after by skilled workmen.

External climatic conditions also exercise great influence on the course of the recuperation process. Dull moist weather lessens the chimney draught, and consequently increases the pressure in the apparatus, and causes loss by leakage; on the other hand, in bright dry weather the draught is better, and the operation goes on more successfully.

(4) *Insoluble Basic Sediment.*—This sediment, which has already been mentioned, consists of a basic salt, insoluble in water but soluble in acids, which is deposited in the storage reservoirs as a viscous, ochreous magma.

The analysis of this salt in its crude condition, merely drained, shows the following composition:—

Sulphur trioxide (SO_3) = 24·43 per cent.
Ferric oxide (Fe_2O_3) = 35·90 „

It also contains a considerable proportion of substances insoluble in HCl, such as silica, earthy matter, lead sulphate, etc.

The sediment retains about 30 per cent. by weight of *rouil.* When washed and dried it contains

Sulphur trioxide (SO_3) = 37·80 per cent.
Ferric oxide (Fe_2O_3) = 43·20 „

When the operation has been properly conducted the amount of sediment does not exceed 8 to 10 per cent. of the total product, but if badly conducted may attain as much as 20 per cent.

If it be remembered that 100 parts by weight of this sediment, as taken from the reservoirs, are equivalent—so far as concerns its content of iron oxide—to 240 or 250 parts of *rouil*, and that it is generally wasted, or at least very difficult to get rid of, it will be evident that the loss attains the enormous proportion of 20 to 25 per cent. of the finished product. Later on we shall see how this can be remedied.

(5) *Cost Price.*—A staff of 2 men is sufficient to work the size of plant we have described—one man to look after the operation, the other taking charge of the recuperation and the packing of the products. They will be able to finish 4 charges a day. The *rouil* is packed in carboys or petroleum barrels. The latter

must first be steamed out, and then carefully washed in order to get rid of the traces of oil. The cost per cwt. of the *rouil* product, packed in casks, amounts to—

Nitric acid (36 Bé.), 4¼ lbs.	= 5d.
Ferrous sulphate, 76 lbs.	= 9½
Sulphuric acid (60 Bé.), 5¼ lbs.	= 1¼
Labour	= 3¼
Lead, coal, etc.	= 2
Management expenses, interest, etc.	= 1
Packing	= 10
Total	2s. 8d.

The sale price averaging 3s. 2d., the nett profit is therefore 6d. per cwt.

B. GESCHWIND PROCESS—EMPLOYMENT OF SODIUM NITRATE, AND RECOVERY OF BYE-PRODUCTS.—This process, the original idea of which is due to M. Gaillot, manager of the Aisne Agricultural Station, is described in the author's (French) Patent Specification, dated 4th August 1897.

It has been in use for more than 12 months at the Chailvet works, with excellent results. We have already seen that the formation of sediment in the reservoirs entails a loss of about 20 to 25 per cent. of the finished product; consequently it is of great interest to be able to prevent the formation of these sub-salts, or at any rate to use them up in the manufacturing process. This has been successfully accomplished in a very simple manner by dissolving the sediment in sulphuric acid, and using up a fraction of the resulting ferric sulphate liquor in each operation.

The saving effected by the use of sodium nitrate is also considerable, and easily expressed in figures. Commercial 36° Bé. nitric acid contains 52·80 per cent. of HNO_3, and may be reckoned worth 10s. per cwt., the HNO_3 being therefore worth 2d. per lb. Commercial nitrate of soda contains 69·80 per cent. of HNO_3, and costs about 7s. 6d. per cwt., consequently the HNO_3 in sodium nitrate costs a little over 1d. per lb., a saving of about one-half. It is therefore advantageous to employ this method, the more so that it is an extremely simple one.

The requisite apparatus is exactly the same as that for the nitric acid process, except for an additional boiling pan made of lead and heated by direct fire or steam, a lead-lined wooden sodium nitrate tank, and tanks for the acid solution of ferric sulphate.

(1) *Dissolving the Sediment.*—This is a very simple operation. About 66 gallons of the slimy sediment are placed in the supplementary pan, which holds about 180 gallons, and, after adding 22 gallons of water and 20 gallons of 60° Bé. sulphuric acid, the whole is raised to boiling, and is kept constantly stirred. The sediment gradually dissolves, and at the end of 2 or 3 hours the liquor is run into tanks to clarify.

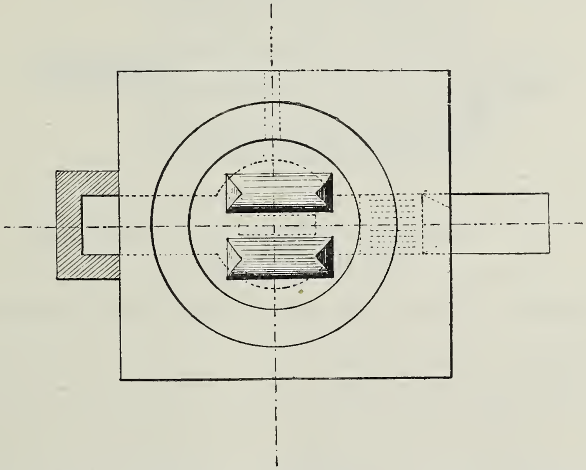

FIG. 182.—Manufacture of rouil mordant. Treatment of sediment. Section of boiling pan.

The solution has a density of 47° to 48° Bé., is greenish brown in colour, and exhibits the following composition per litre :—

Average.	Constituents.	1	2	3	4	5	6
395 grms.	Sulphur trioxide (SO_3)	429	430	409	428	312	360 grms.
180 ,,	Ferric oxide (Fe_2O_3)	172	188	205	187	134	185 ,,

In the manufacture of *rouil* 100 vols. of this liquor represent 12 of 60° Bé. sulphuric acid.

It may also be employed for other purposes, and—prepared either in the aforesaid manner or by peroxidising ferrous sulphate with nitric acid or sodium nitrate, in presence of the necessary amount of sulphuric acid—is utilised for coagulating blood from slaughter-houses, and converting the same into a non-putrefactive manure.

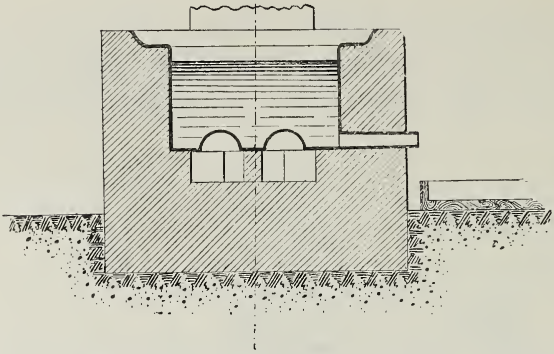

Fig. 183.—Manufacture of rouil mordant. Treating the sediment. Section of boiling pan.

(2) *Dissolving the Sodium Nitrate.*—This operation is conducted in a leaden pan, the salt being stirred up in hot water and left to cool, thus furnishing a saturated 40° to 42° Bé. solution containing about 680 grms. of sodium nitrate per litre, and serving to replace nitric acid in the peroxidation of ferrous sulphate.

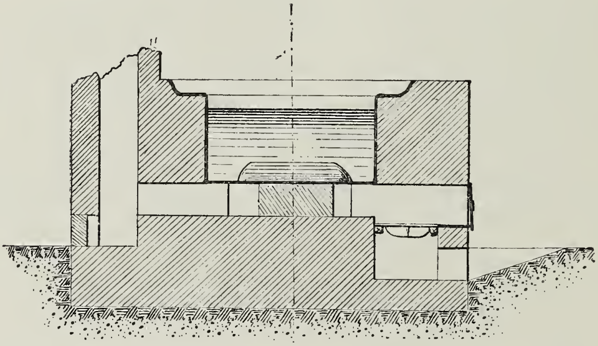

Fig. 184.—Manufacture of rouil mordant. Treating the sediment. Section through boiling pan and fire-place.

(3) *Manufacturing Details.*—The peroxidation vat is charged with 22 gallons (about 330 lbs.) of the acid solution of ferric sulphate, prepared from the *rouil* sediment as just described, together

with about 5 gallons of the nitrate solution (equal to 33 lbs. of sodium nitrate) and enough sulphuric acid (2·6 to 2·9 gallons of 60° Bé. acid) to form sodium bisulphate with the base of the latter salt. Heat being then applied, the ferrous sulphate is added by degrees, and the operation is conducted in exactly the same manner as in the nitric acid process, namely, adding part of the recovered liquor when the reaction slackens, and stopping the supply of ferrous sulphate as soon as the evolution of nitric oxide ceases. The recuperation process is also the same as before.

The *rouil* so obtained contains a little sodium bisulphate—about 46 lbs. from a charge of the above dimensions, but insufficient to affect the quality of the product.

Owing to the employment of the recovered ferric sulphate from the sediment, a greater weight of product is obtained for a given consumption of nitric acid and ferrous sulphate; consequently the cost of manufacture is reduced, and works out as follows per cwt. of product:—

		s.	d.
Sodium nitrate, 2·65 lbs. at 7s. 6d. per cwt.	=	0	2
Ferrous sulphate, 64 ,, 1s. 0d. ,,	=	0	7
Sulphuric acid, 8½ ,, 2s. 6d. ,,	=	0	2
Labour		0	3
Coal, lead, etc.		0	2
Packing		0	10
Management expenses, interest, etc.		0	1
Total		2s.	3d.

Since the cost in the nitric acid process is 2s. 8d., we have here an extra profit of 5d. per cwt., *i.e.* 11d. instead of 6d.—a decided advantage.

C. CHARACTERISTICS OF *ROUIL*.—The colour of the *rouil* liquor is deep reddish brown by reflected light, rusty by transmitted light. A blackish, greenish, or yellow tinge indicates defective manufacture, being due either to fixation of the nitrous fumes by ferrous sulphate, or to an excess of the latter or of sulphuric acid.

In the first-named case, and when the defect is considerable, it may be remedied by adding sulphuric acid in larger excess and applying heat. Red fumes and a characteristic effervescence will be suddenly produced, and when the liquor is again quiescent the black coloration will have disappeared.

In the second case, the liquor, after acidification with H_2SO_4, evaporation to almost dryness, and abundant dilution with water, will decolorise potassium permanganate. When the excess of ferrous sulphate is considerable, the liquor will give off red fumes on being treated with nitric acid in the warm.

When diluted with a large excess of distilled water *rouil* liquor throws down a precipitate of an insoluble and highly basic ferric salt, leaving a more acid ferric salt in solution, the reaction being more pronounced if the water contain calcium carbonate. It is on this property that the fixing of the ferric oxide by the fibre in mordanting silk (*rouillage*) is based.

Commercial *rouil* is of 40° to 46° Bé. density. It is of merely relative stability, and tends to separate into an insoluble basic salt and a soluble acid salt when stored for some months. It often contains organic matters introduced by the ferrous sulphate; and these substances, incompletely destroyed by the nitric acid during the peroxidation process, are gradually oxidised by the ferric sulphate, which is thereby reduced to the ferrous state. This reaction is accentuated by light.

A *rouil* of good quality should not contain ferric chloride, this salt being of no use in mordanting silk. The liquor should therefore give no precipitate with silver nitrate.

The following table shows the percentage composition of several varieties of commercial *rouil*, Nos. 1, 2, and 3 having been prepared by the sodium nitrate process, the others by the nitric acid method:—

Constituents.	1	2	3	4	5	6	7	8	9
Ferrous sulphate, $FeSO_4, 7H_2O$.	0·17	...	2·00	1·53	...	...	0·38	1·70	...
Total ferric oxide, Fe_2O_3	15·85	14·30	15·00	17·09	14·74	15·80	14·80	14·10	14·50
Sulphur trioxide, SO_3	19·10	19·20	20·00	19·99	20·40	21·20	21·40	21·30	20·40
Sodium bisulphate, $NaHSO_4$ . . .	1·85	1·70	2·30	...	...	...	...	...	...
Density, Baumé .	45°	44°	45°	46°	42°	44·5°	45°	45°	44°

PART III

USES OF THE SULPHATES OF ALUMINIUM AND IRON

CHAPTER V

USES OF ALUMINIUM SULPHATE AND ALUMS

§ 1. APPLICATION TO THE ART OF DYEING

120. **Introduction.**—It is very evident that the two most essential elements in dyeing are the materials, and the dye stuffs with which they are to be treated. There is also, however, a whole series of substances—the mordants—of considerable importance from the part they play in fixing the dye stuff on the fibre, or in modifying the shade of colour obtainable. Chief among them are the aluminium mordants, which have been from time immemorial, and still are, employed for all kinds of fibre.

The different alums, with ammonium, potassium, or sodium as their base, have been the most widely used in dyeing, not only because they are themselves mordants, but also because they serve for the production of other aluminium mordants—aluminium acetate, sulpho-acetate, etc. They are still largely employed, the best qualities being in the form of large vitreous crystals entirely free from iron.

Alum is, however, becoming more and more displaced everywhere by aluminium sulphate, which is now obtainable fairly pure in commerce and in a state suitable for the preparation of all the other aluminium mordants. It is besides more economical than alum, the latter containing barely 10 or 11 per cent. of the really active ingredient, alumina, whereas the well-made sulphate, exempt from iron, contains 16 to 17 per cent. without being any dearer.

When a solution of normal aluminium sulphate is partly neutralised by adding sodium carbonate or bicarbonate, chalk, etc., solutions of *basic aluminium sulphates* are formed.

These new salts vary in composition according to the degree of neutralisation, as the following equations will show:—

(1) $Al_2(SO_4)_3 + 2NaHCO_3$
$= Al_2(HO)_2(SO_4)_2 + Na_2SO_4 + 2CO_2$,

(2) $2[Al_2(SO_4)_3] + 6NaHCO_3$
$= (Al_2)_2(HO)_6(SO_4)_3 + 4Na_2SO_4 + 6CO_2$,

(3) $Al_2(SO_4)_3 + 4NaHCO_3$
$= Al_2(HO)_4(SO_4)_4 + 2Na_2SO_4 + 4CO_2$.

The first of the foregoing basic sulphates is probably the one most widely used.

When solutions of basic aluminium sulphates are boiled a still more basic and insoluble salt is thrown down, especially in presence of textile fibres, and a normal, or even acid, salt remains in solution. Similar changes evidently occur when the fibres impregnated with these solutions are dried; and it is upon these facts that the employment of basic salts in mordanting is founded.

Experience teaches that the more basic the solution the more readily is it decomposed, whether by heat or dilution with water, and the larger the proportion of alumina fixed upon cotton fibre by immersion and subsequent drying at a low temperature.

When caustic alkalis, or carbonates of the alkalis or alkaline earths, are added to normal solutions of alum, products known as *neutral* or *basic alums* are obtained. These are analogous to the basic aluminium sulphates just mentioned, and their solutions when heated and diluted decompose and furnish analogous precipitates (Hummel and Dommer). The manner of using alums and aluminium sulphate as mordants is the same, and both compounds should be free from iron.

121. **Application to Cotton.**—The best method is that of *precipitation*, the fibre being impregnated uniformly with basic aluminium mordant, dried, and entered in a solution of some salt

capable of fixing the alumina on the fibre, either by precipitation in the form of oxide or by combination to form an insoluble compound. A number of substances can be employed for this purpose, such as ammonium carbonate, sodium phosphate, sodium arsenate, sodium silicate, soap, ammoniacal sulphoricinate, etc. In every case the fixing agent, degree of concentration, temperature of bath, and duration of exposure must be accurately determined by experiment.

122. **Application to Wool.** — Normal aluminium sulphate alone is used for mordanting wool, the basic salt being too readily decomposed, the result of which would be superficial mordanting, dulness of colour, incapacity to stand the effects of friction, and harshness of touch.

The solution must be boiling hot in order to expel the air in and around the wool-fibre, as also to soften the fibre and render it thoroughly permeable. It is also desirable to add a certain quantity of potassium bitartrate, since this increases the depth and brightness of the subsequent colour, prevents the ready and superficial precipitation of alumina by the ammonia proceeding from the wool, and increases the amount fixed on the fibre.

To successfully mordant 10 grms. of wool with aluminium sulphate, 0·8 grm. of this salt and 0·7 grm. of potassium bitartrate (cream of tartar) are dissolved in 1 litre of water. The wool is entered into the cold liquor and the temperature is raised to boiling point within 1 to 1½ hours, and, after being maintained thereat for 30 to 60 minutes, the fibre is carefully washed (Hummel and Dommer).

123. **Application to Silk.**—The aluming of silk may be performed anterior to or during the operation of dyeing. In the former event the alum bath may be kept going continuously, whereas in the latter case it generally has to be thrown away after use.

The silk being made up into *bâtons*, is put through three or four stretchings and steeped for several hours in the alum bath, being generally entered in the evening and left over night. The bath should be cold-saturated, and is replenished from time to time with a boiling concentrated solution of alum—or the same result may be obtained by keeping a bag full of alum crystals in one end of the bath and stirring up well after each passage of the silk.

For this, as in all the other operations of dyeing, the silk, whether raw or boiled, should always be properly moistened beforehand, *i.e.* should contain about its own weight of water, a result obtained by wringing it well. If introduced dry, the silk dyes badly, and in some cases absorbs the bath liquor with difficulty. It follows that this degree of moisture causes the permanent baths to undergo corresponding dilution; hence the necessity for replenishment with concentrated liquor in order to keep up their standard strength.

The alum bath should be cold. On leaving the bath, the silk should not be allowed to dry or it will become harsh to the touch and difficult to moisten again; in fact, another passage through the alum bath will be necessary. After being well drained the silk is rinsed slightly with running water and, if necessary, beaten (coarse silks).

Only a very little alumina is fixed on the silk by aluming, and even this amount is so by the action of the rinsing water, which should preferably be calcareous, calcium bicarbonate assisting to precipitate alumina on the fibre (M. Moyret, *Traité de la teinture des soies*).

Silks that have already been dyed are alumed in the same way; the bath may perhaps be warmed up a little, and is generally used but once.

Aluminium sulphate is used in the same manner, the alumina being usually fixed by a slight rinsing with water and a brief sojourn in a cold bath of sodium silicate (density, 1·005), followed by careful washing. The use of basic aluminium sulphate may spoil the brilliancy of the resulting shades.

124. **Preparing and Using Aluminium Acetates.**—Normal aluminium acetate may be obtained in solution by dissolving alumina in acetic acid, or by adding lead acetate solution to dissolved aluminium sulphate in the proportion indicated by the equation

$$Al_2(SO_4)_3,\ 18H_2O + 3[Pb(C_2H_3O_2)_2,\ 3H_2O] = Al_2(C_2H_3O_2)_6 + 3PbSO_4 + 27H_2O.$$

From this normal salt a series of basic aluminium acetates can be obtained by treating the solution with increasing quantities of an alkali carbonate.

The solutions of these basic acetates, *containing sodium acetate*, are precipitated by heat, the higher the basicity the lower the temperature required for dissociation. Curiously enough, however, this temperature is higher the more dilute the solution; mere dilution alone will not cause precipitation.

Freshly prepared solutions of pure aluminium acetate (equivalent to 200 grms. of ordinary sulphate per litre) are not precipitable either by heat or dilution; but when left at rest for a certain time they decompose spontaneously, alumina being deposited.

All solutions of the various aluminium acetates, whether normal or basic, are precipitated by heat when diluted, if they contain sulphates such as potassium or aluminium sulphate, etc. This is always the case with the basic acetates, made from aluminium sulphate, when a portion of the lead acetate is replaced by alkali carbonates—

$$Al_2(SO_4)_3, 18H_2O + Na_2CO_3 + H_2O + 2[Pb(C_2H_3O_2)_2, 3H_2O]$$
$$= Al_2(C_2H_3O_2)_4(HO)_2 + Na_2SO_4 + 2PbSO_4 + CO_2 + 24H_2O.$$

The result is the same, whether the sodium carbonate is added before or after the lead acetate. When a solution of normal aluminium acetate containing sulphates is precipitated by heat, the precipitate re-dissolves on cooling; but under no circumstances does this happen with the basic acetates. The precipitate formed in presence of sulphates is an aluminium sulphate containing a large excess of the base.

Experience has shown that when cotton is impregnated with a solution of normal aluminium acetate (= 200 grms. of normal sulphate per litre), and then dried at a low temperature, about 50 per cent. of the alumina present is fixed on the fibre; and an equivalent solution of the basic salt $Al_2(C_2H_3O_2)_4(HO)_2$, containing sodium sulphate, will, under the same conditions, give up nearly the whole of its alumina.

Aluminium acetates (especially the normal salts) prepared with lead acetate are liable to contain a little lead sulphate.

For this reason, lead acetate may be advantageously replaced by an equivalent quantity of calcium or barium acetate when the presence of this sulphate would be injurious.

It has long been known that no practical advantage accrues from using enough lead acetate to decompose the whole of the aluminium sulphate. According to Koechlin, this is explainable by the assumption that the actual mordant fixed on the fibre is not pure alumina, but probably in most cases an insoluble basic aluminium sulphate.

An excellent mordant may be prepared by dissolving insoluble basic aluminium sulphate in hot acetic acid. The basic sulphate is easily obtained by carefully neutralising a solution of alum by sodium carbonate, until the precipitate first formed ceases to re-dissolve.

This method is due to Koechlin. Aluminium sulphate may also be used, and the resulting mordants are known as *aluminium sulpho-acetates*, their formation being shown by the following equations:—

(1) $Al_2(SO_4)_3,\ 18H_2O + 2[Pb(C_2H_3O_2)_2,\ 3H_2O]$
$= Al_2SO_4(C_2H_3O_2)_4 + 2PbSO_4 + 24H_2O,$

(2) $Al_2(SO_4)_3,\ 18H_2O + 3[Pb(C_2H_3O_2)_2,\ 3H_2O] + 2NaHCO_3$
$= Al_2SO_4(C_2H_3O_2)_3,\ HO + 3PbSO_4 + Na_2SO_4 + 2CO_2 + 45H_2O.$

Experience has shown that the more basic these sulpho-acetates the lower their decomposition point, whether by heat or dilution, *i.e.* their sensitivity is increased.

Aluminium sulpho-acetates yield up nearly all their alumina to cotton fibre after impregnation and drying. In this particular they act more strongly than aluminium sulphates, and almost the same as basic aluminium acetate—

$$Al_2(C_2H_3O_2)_4(HO)_2.$$

The technical name applied to the various acetates and sulpho-acetates of aluminium employed in dyeing is "red mordant," because they are universally used for printing and dyeing alizarine reds on cotton. Commercial red mordant is prepared by the double decomposition of normal aluminium sulphate and commercial calcium acetate. It contains a certain amount of undecomposed aluminium sulphate, and is an impure sulpho-acetate; the variety known as "red tin mordant" is one where the decomposition has been effected as completely as possible, and which consequently represents an impure normal aluminium acetate.

These mordants are chiefly used for *cotton*, and especially for *calico printing*. The mordant solution is thickened with flour, starch, dextrin, etc., and is then printed on the cotton and dried. The cloth, in a more or less open and stretched condition, is afterwards exposed to the air under suitable conditions of temperature and humidity.

Next follows *fixing* or *dunging*, an operation consisting in passing the goods through hot liquors containing cow's dung, sodium arsenate, sodium phosphate, sodium silicate, chalk, etc. The object of this treatment is threefold, namely—

(1) To more thoroughly fix on the fibre that part of the mordant which has escaped the influence of the air during the stretching process.

(2) To prevent the subsequent staining of the unprinted portions through the running of the soluble mordant.

(3) To remove the thickening materials.

Aluminium acetates are largely used for the so-called "steam colours," and frequently serve to replace basic aluminium sulphates in "Turkey-red dyeing." On the other hand, they are rarely employed for common fabrics, since under the ordinary conditions of fixation they offer no advantage over the basic sulphates, and are more costly. They cannot be used for mordanting *wool*, owing to their low stability; and are but seldom employed for *silk*, except in printing (Hummel and Dommer).

125. **Employment of Aluminium Sulphate in Carbonising Wool.**—Wool is frequently contaminated with vegetable impurities, which are very difficult to entirely remove by mechanical means, and are a source of great trouble in the dyeing process when present in piece goods.

It was proposed by R. Joly, of Elbeuf, to destroy these impurities with aluminium sulphate, and the method was afterwards adopted by many cloth manufacturers of Elbeuf, Sedan, Châteauroux, Romorantin, Mazamet, etc., it having been found possible by this means to carbonise fabrics dyed with fugitive tints (*Rev. Ind. et Sciences Chim.*, 1879, p. 69).

Aluminium chloride can be prepared from aluminium sulphate by simply treating the latter with calcium chloride, which is cheap and easily procured. The dissolved aluminium chloride is easily separated from the precipitated calcium sulphate by filtration, alone or assisted by pressure (filter-press). The solution employed in carbonising has a density of about 5° Bé. for delicate tints, or 7° Bé. for darker shades. The fabric is immersed in and thoroughly impregnated with the solution, and is afterwards drained in the hydro-extractor—whether loose wool, yarn, or cloth—dried at 60° to 100° C., and carbonised at 120° to 135° C. Under the influence of this temperature the chloride reacts on the vegetable impurities, and decomposes them without altering the dyes or the animal fibre in the least. All that is necessary is to shake, stir, and beat the material, and the carbonised matter will come out as dust. The operation should be followed by a thorough scouring; and the material should be carefully washed before entering the aluminium chloride bath (Pommier, article on "Alum" in Fremy's *Encyclopédie*).

§ 2. EMPLOYMENT IN THE MANUFACTURE OF PIGMENTS

126. **The Manufacture of Lake Pigments.**—A "lake" pigment consists of a solid material, or "*base*," generally white, tinted by some colouring matter.

Sometimes the base is coloured direct, as if the dyeing of a fabric were in question; but generally the base and pigmentary matter are precipitated together, so as to produce the most intimate combination possible between them.

The production of lakes is a delicate operation, and a matter of great importance.

Artists employ several handsome and durable lake colours (madder lake, weld lake, etc.).

Paper stainers use a large quantity of lakes, often rather fugitive (redwood lakes, aniline lakes, etc.).

Cloth printers are also large consumers of fustic lakes, alizarine lakes, etc., the colours being dissolved in acetic acid, and the solution, after being thickened, is printed in the ordinary manner. The cloth is afterwards steamed to drive off the acetic acid and fix the colouring matter on the fabric.

The *base* most frequently employed in the production of lake pigments is *alumina*, either alone or in combination as various salts, mostly of a basic character.

Alumina is often employed as *gelatinous alumina*, precipitated by a slight excess of ammonia from a solution of alum or aluminium sulphate.

Gelatinous alumina readily absorbs pigments, and is stained directly by a decoction of cochineal, redwood, weld, etc.; but more often the resulting lakes are deficient in brightness, and moreover, when dried they become hard, horny, and difficult to thin down with water or oil.

In manufacturing lake pigments the basic aluminium sulphate corresponding to the formula $Al_2O_2SO_4$ is most frequently used. This salt is insoluble in water; it is pure white and opaque, instead of being transparent like gelatinous alumina.

It is easy to collect and wash, and when dried furnishes a very white friable product, not hard or horny.

This basic sulphate is prepared by saturating a solution of alum or aluminium sulphate with sodium carbonate until a light persistent precipitate is formed. Constant agitation is kept up during the operation, and the clear liquid is separated from the precipitate. This liquid when boiled deposits the basic sulphate, which is then washed by decantation.

In order to obtain a product of known composition, the solution of alum or aluminium sulphate may be precipitated with sodium carbonate until the reaction becomes alkaline, indicating that the whole of the alumina is precipitated. This operation gives the quantity of sodium carbonate necessary for the complete saturation of the sample. The operation is then repeated, taking only two-thirds of the quantity of sodium carbonate thus indicated. The reaction is as follows:—

$$Al_2(SO_4)_3 + 2Na_2CO_3 = 2CO_2 + 2Na_2SO_4 + Al_2O_2SO_4.$$

Generally the precipitation of the basic sulphate is not effected separately, but is combined with the incorporation of the pigments.

Sometimes alumina, or the basic salt precipitated from alum or aluminium sulphate by metallic zinc at boiling temperature, is used.

Sodium aluminate is also largely employed. The salt is mixed with a decoction of the pigment, and the product is thrown into a solution of aluminium sulphate, the precipitated alumina carrying down the colouring matter.

Various other insoluble salts of aluminium, such as phosphates and, above all, the borate, are used as bases for lake pigments. The advantage of this is that the borate, for example, can be prepared from aluminium sulphate and borax. The latter salt having only a feeble alkaline reaction, does not affect the pigments that are sensitive to alkalis, such as cochineal, redwood, etc.

Insoluble aluminates, and notably *magnesium aluminate*, also serve for the preparation of lake pigments.

Magnesium aluminate is obtained by gradually adding ammonia to a solution composed of

Potassium alum	45 grms.
Magnesium sulphate	13 ,,
Ammonium chloride	6 ,,

dissolved in 250 c.c. of water. The aluminate precipitated carries down nearly all the magnesia. By adding to the solution some pigment, such as a decoction of cochineal, a handsome lake will be produced, provided an excess of ammonia is avoided.

Stannic acid combines readily with pigments, and forms the basis of most lakes employed in cloth printing.

Sodium stannate may be used to prepare lakes on a stannic acid basis. The method is similar to that used for sodium aluminate, a solution of the pigment in sodium stannate being precipitated by dichloride of tin. Sometimes aluminium sulphate is used to precipitate the sodium stannate, in which case a true aluminium stannate, representing the base of the lake, is formed.

Antimonic acid, antimony oxide, tungstic acid, oxides of lead, zinc, chromium, magnesium, calcium, etc., also serve as bases for certain lakes, as also chalk, albumin, gelatin, and even starch or flour. This need not be further discussed.

For paper staining and cloth printing the lakes are sold in paste forms, and are thus easy to use. These generally contain 33 per cent. of water.

For use as artists' colours, the lakes are generally supplied in lozenges. For making these on a small scale the paste is put in a funnel, into the stem of which is inserted a glass rod. By pressing on this rod the paste is forced out in the shape of small conical heaps, which are then placed on sheets of glass and dried in a stove at a low temperature. The dried blocks separate easily from the glass.

The lakes are also frequently supplied in the form of dry powder, which is more simple and is free from inconvenience when they have to be ground in oil or water (Guignet, article on "Colour Making" in Fremy's *Encyclopédie*).

127. **Yellow Lakes.** — *A*. WELD LAKE. — Weld (*Reseda luteola*) is an indigenous plant which was formerly grown on a large scale for dyeing purposes, but is now almost gone out of use.

The pigmentary principle of weld is luteoline, discovered by Chevreul. Luteoline is almost colourless, but turns deep yellow under the influence of a powerful base; it crystallises in beautiful needles, and behaves as a weak acid. It is only sparingly soluble in boiling water, but dissolves in considerable quantity in water at 200° under pressure. For the production of weld lake, well-harvested and dry plants—not those browned by exposure to rain, air, and light—are selected. Plants that remain slightly green when dry are just as good as those of a pure yellow colour.

The plant is cut into small pieces and left in water for 12 hours. It is then boiled and a weight of alum equal to that of the weld is added, the liquid being then boiled up for a few minutes, filtered through a cloth, and afterwards precipitated by sodium carbonate solution so as to throw down a basic aluminium sulphate. The pigment is carried down with the precipitate, which has merely to be collected, washed by decantation, and dried at gentle heat.

Another process consists in preparing a white base by boiling

1 kilo. of pure chalk in 1 litre of water and adding 100 grms. of powdered alum. Brisk effervescence ensues; the mixture is stirred and a decoction of weld is added by degrees until no more of the pigmentary principle is absorbed. The mother liquor separated from the lake serves for treating a fresh quantity of weld.

Weld lake is the most durable of all the yellow lakes, and is the only one suitable for use as an artist's colour (Guignet).

B. YELLOW (*STIL DE GRAIN*) LAKE. — This is a lake of somewhat complex composition, and is only used for theatrical decorations, floor-staining, etc. It is not very stable.

The chief ingredients of this lake are " French berries " (*graine d'Avignon*, the fruit of *Rhamnus infectorius*) and " Persian berries " (from *Rhamnus saxatilis*), to which are added quercitron, weld, fustic, safflower, curcuma—all freshly gathered.

The decoction is treated with alum or aluminium sulphate, and filtered, the filtrate being then mixed with finely powdered chalk and the whole stirred briskly to facilitate the liberation of carbon dioxide.

C. OTHER YELLOW LAKES of fine appearance, but deficient in permanence, are prepared from *quercitron*, the bark of an American oak (*Quercus nigra*) (Guignet).

128. **Red- and Rose Lakes.**—*A*. MADDER OR ARTIFICIAL ALIZARINE LAKES.—A great variety of tone can be obtained from madder lakes, ranging from light rose-red to deep violet, almost black, through the entire scale of reds.

The lighter shades can be easily prepared by adopting the following precautions:—

When madder is used it is extracted with cold water, in order to remove all the extraneous substances (gums, sugars, albumin, etc.) likely to injure the preparation of the lake. Most of the methods in use are based on the property exhibited by alizarine of dissolving in a hot solution of alum, in which particular the artificial alizarine is especially distinguished. For rose-red lakes the variety known as *alizarine for reds* is used, *alizarine for violet* being taken for violet and purple-brown lakes. Both substances are obtainable in the form of yellow-brown liquid paste, very sparingly soluble in water but soluble in alcohol. Alkaline solutions dissolve alizarine and furnish a fine red liquid; alum gives a slightly yellowish solution, and if the operation is conducted at boiling temperature a portion of the alizarine deposits on cooling. Besides, it is better not to boil madder or alizarine in presence of alum solution; a temperature of 40° to 50° C. is quite sufficient for the saturation of a solution of 1 part alum in 10 to 12 parts water with alizarine.

After cooling the liquid down to 35° to 40°, a solution of sodium carbonate is gradually added, with continual stirring, not more than $\frac{2}{3}$ as much sodium carbonate as would fully saturate the alum being used. By this time the liquor will have become a deeper red in colour, and when heated to boiling will throw down basic aluminium sulphate, which carries the alizarine down with it and forms a fine dark rose-red lake, even when dried.

According to Persoz, this lake offers the advantage of complete solubility in acetic acid, on which account it can be used in cloth printing. The same author also gives another method of preparing this lake, namely, by adding sub-acetate of lead to a solution of alum saturated with alizarine at 30° or 40°. An abundant precipitate of lead sulphate is formed, and on filtration is separated from the dark red liquor, which when boiled deposits the lake in question. The most suitable proportions to use appear to be equal weights of alum and (solid) sub-acetate of lead. The residual mother liquor will serve for dissolving a fresh quantity of alizarine.

A handsome lake is obtained by dissolving alizarine in water containing a very little ammonia, and by adding gradually thereto a 10 per cent. solution of alum. This lake is of a dark red colour. In the same manner a very dark violet, or even nearly black, lake can be prepared by adding ferric sulphate to the alum, or by using ferrous sulphate by itself.

Kopp has described a very ingenious process consisting in treating madder with a solution of sulphurous acid. This gives a solution of alizarine, which when heated with saturated alum solution furnishes a lake of good quality.

Nowadays madder lakes are very little used, their place having been taken by lakes made from artificial alizarine and purpurine.

These lakes are often adulterated, the red kinds often containing cochineal, redwood, fuchsine, eosine, safranine, etc.; and the violet or black lakes, campeachy, archil, aniline violet, etc. (Guignet), constituting adulterations difficult of detection.

B. COCHINEAL LAKES.—The mother liquors from the manufacture of carmine are often used for making these lakes, being employed to thin down gelatinous alumina or basic aluminium sulphate, or mixed with alum and boiled after saturation with sodium carbonate.

It is, however, preferable to work with fresh materials, and to boil the ground cochineal in water containing potassium bitartrate. The extract is filtered and treated with powdered alum, a little tin protochloride being added drop by drop when solution is complete. After a while a very fine quality lake is deposited, and, when this has been collected, a second lake, of inferior quality and lighter colour, can be recovered by precipitating the mother liquor with sodium carbonate (Guignet).

The cochineal lakes, known as *carmine lakes*, are often adulterated with chalk or starch.

Very handsome rose-red lakes are easily prepared by dissolving *ammoniacal cochineal* in water, filtering the solution, and precipitating with saturated alum.

Ammoniacal Cochineal in tablets is also a lake prepared in a special manner. Three parts of ammonia and 1 of cochineal are macerated for a month in a closed vessel, the clear liquid being then drawn off and mixed with 0·4 part of gelatinous alumina. The whole is evaporated in a copper vessel until all smell of ammonia has disappeared, whereupon the thickish mass is cut up into tablets and dried (Wurtz's *Dictionary*).

C. LAC LAKE.—The raw material for this product is *stick lac*, the thick, hard, adherent incrustation surrounding the twigs of certain large fig trees or mimosæ, and consisting mainly of a mixture of resins enclosing cells wherein are imprisoned certain gall insects (*Coccus lacca*) which yield a red pigmentary matter (carminic acid).

To prepare lac lake, a decoction of stick lac in weak caustic soda is precipitated with alum.

Lac lake contains—

Pigmentary matter	50 parts,
Resins	40 ,,
Alumina	9 ,,
Extraneous matter	1 ,,

For use, this aluminous lake is dissolved in hydrochloric or sulphuric acid (Wurtz's *Dictionary*).

D. REDWOOD LAKES.—There are several varieties of redwood, namely, Pernambuco wood (*Cæsalpinia crista*); Brasil wood (*C. brasiliensis*); Sapan wood (*C. sappan*); Brasilette (*C. vesicaria*), the latter being the least valuable; and, from these woods, lakes are prepared on a base of stannic acid, antimony, oxide, etc.

Venetian Ball Lake is obtained by incorporating gelatin and gelatinous alumina in Brasil extract, the latter being renewed until no more colouring matter is taken up. The colour is then brightened by the action of alum, or turned violet by means of soap solution. *Italian Lake* is prepared by mixing a decoction of redwood with alum, followed by chalk to partly neutralise the latter and throw down alumina, which fixes the colouring matter.

Basic aluminium sulphate or previously saturated alum, which will throw down the sulphate when heated, can also be used. Starch paste is sometimes added to redwood lakes, especially when they are to be used in making fancy papers.

Although not very fast colours, the redwood lakes are largely used by paper stainers for marbling fancy papers, etc., as well as for theatrical decorations (Guignet).

E. ANILINE RED LAKES.—Several very handsome and fairly durable lake pigments of this class are prepared from various artificial dye-stuffs.

129. **Green Lakes.**—These are merely mixtures of yellow and blue lakes, so as to produce transparent greens; fustic lake and Prussian blue, for example, furnishing very handsome green shades, though not very fast.

130. **Violet Lakes.** — As already stated, violet lakes are prepared from madder; and very fine ones can also be obtained from campeachy and tin dichloride.

Very good violet lakes for coloured and fancy paper are now made, from aniline violet, by employing an aqueous solution of this violet to colour a *white base* formed of basic aluminium sulphate combined with gelatin. Sometimes, also, small quantities of tannin and starch are added.

The finest compound violets are obtained with Prussian blue and madder or cochineal lakes (Guignet).

131. **Application of Aluminium Sulphates to the Manufacture of Prussian Blue.**—Prussian blue is made by a very simple process, namely, precipitating a solution of potassium ferrocyanide, or yellow prussiate, with a salt of iron, under suitable conditions.

Prussian blue in the pure state is inapplicable for most purposes in painting, and consequently the commercial varieties contain extraneous substances, not always with intent to defraud. Thus the addition of an aluminium compound at the moment of precipitation seems to improve the product. For this purpose alum is mixed with the iron sulphate used, and the resulting aluminium ferrocyanide, which resembles alumina, remains intimately mixed in the mass.

For best quality Prussian blue, 1 part of alum is used to every 7 or 8 parts of iron sulphate, whilst for the lower grades the proportion is increased to 1 : 2–3 ; and for the lowest of all, equal parts are used. The alum may be advantageously replaced by an equivalent quantity of aluminium sulphate (Guignet).

Mineral Blue or *Antwerp Blue* is a kind of Prussian blue adulterated in the process of preparation, magnesium sulphate and zinc sulphate—which form a white precipitate with potassium ferrocyanide—being added in addition to alum.

132. **Application of Aluminium Sulphates to the Manufacture of Thénard Blue.** — This pigment has now almost entirely gone out of use ; nevertheless, it is of considerable historic interest, being the first cobalt blue pigment ever used as an artist's colour.

It is prepared by precipitating a solution of cobalt chloride or nitrate by tribasic sodium phosphate, which gives a somewhat violet-tinged, rose-red, gelatinous precipitate of tribasic cobalt phosphate. After careful washing, the phosphate is intimately mixed with gelatinous alumina—prepared by adding an excess of ammonia to a solution of alum, or aluminium sulphate free from iron, and washing the precipitate.

The mixture is dried in the oven and calcined at cherry-red heat in a closed crucible. The proportions given by Thénard are:—1 part of tribasic cobalt phosphate, in the condition of paste (with 30 per cent. of moisture), and 8 parts of gelatinous alumina (Guignet).

133. **Employment in the Preparation of Mars Yellow.**—Bourgeois employed alum in the preparation of *Mars yellow* by precipitating a mixture of ferrous sulphate and alum with sodium carbonate. The handsome golden yellow-brown precipitate assumes various tints under the influence of a longer or shorter calcination.

134. **Employment in the Manufacture of Indian Yellow.**—Analysis having revealed euxanthic acid, alumina, and magnesia as the essential constituents of Indian yellow, attempts have been made to reproduce this compound by artificial means. With this object a solution is prepared of

Potassium alum	45 grms.
Magnesium sulphate	13 ,,
Ammonium chloride	6 ,,

in 250 c.c. of water, and to this solution is added euxanthic acid dissolved in a minimum quantity of ammonia. A yellow precipitate is formed of inferior brightness to the natural Indian yellow.

§ 3. VARIOUS APPLICATIONS OF ALUMINIUM SULPHATES

135. **Employment in the Hide and Leather Industry.**—Attempts have been made at tanning with aluminium salts with or without soap, but the results were not very satisfactory. The method, which was based on the fact that alum or aluminium sulphate will, like tannin, form insoluble compounds with gelatin, gave merely imitation leathers, and, despite numerous attempts, no one has yet succeeded in producing good saddle leather by this means.

On the other hand, alum is successfully applied to the preparation of leather by *ordinary* and *Hungarian tawing*, the last-named process being practised on the thick hides of buffaloes, oxen, and horses to produce white leather for saddlery and harness making. For this purpose the hides are scraped with knives and placed in a soak of alum and brine, and are then beaten to expel a portion of the *coriin* extracted by the brine. The alum acts as a plumping liquor, by virtue of its acid properties and its astringent, antiseptic qualities. On leaving the soak the hides are dried, heated in an oven, and greased with tallow.

If the proportion of common salt exceeds 3 molecules to 2 of alum the latter is decomposed into aluminium chloride, which remains in the hides, and into sodium sulphate, which diffuses in the bath liquor.

In the Hungarian tawing process the alumina—whether present as sulphate or chloride—does not combine with the animal matter; and a washing with water is sufficient to dissolve it and regenerate the hide, which is then readily gelatinised by boiling in water (F. Jean).

Tawed skins are mainly used for boot and glove making, those of the goat, kid, sheep, and lamb especially being treated for the latter purpose.

The dry skins to be tawed are soaked for a period depending on their thickness and degree of dryness. After removing adherent flesh they are unhaired—either by lime or sodium sulphate—then scraped and rinsed in a tub. The next stage consists in immersing the skins for 6 to 12 hours in water containing the putrefied excrement of dogs or pigeons, in order to dissolve out any lime they may have retained, as well as to plump them, render them supple, and fit them for receiving the dressing. After this follows steeping for 3 days in a vat containing water at 30° to 35° C. with bran and flour, the skins being subjected every day to a fulling process, rinsed, and scraped to remove particles of flesh. The *dressing*, which corresponds to the tanning process in other leathers, is effected by fulling the skins in a lukewarm mixture of brine, flour, egg yolks, alum, and water until they are uniformly impregnated and of equal thickness throughout. They are next doubled, flesh-side inwards, dried as quickly as possible, and packed in bundles. Finally, they are streaked and pared to supple them and remove residual traces of dressing paste and flesh; and when rinsed and air-dried are ready for dyeing.

In the German method of dressing skins, which differs from the French process in employing stronger limings, dispensing with the bran soak, and by employing a supplementary treatment with the softening iron and fulling mill, the following soak is used for 1000 skins:—

Flour	27½ lbs.
Alum	27½ ,,
Common salt	11 ,,
Fresh eggs	10 galls.
Milk	0·9 ,,

with sufficient water to form a stiff paste (F. Jean).

136. **Employment in Paper-making.**—Paper made from rags or the various other materials employed cannot be used for writing unless the pulp is mixed with certain substances to bind the fibres together, stop up the pores, etc. The paper has therefore to be glazed. Formerly gelatin was employed for this purpose, particularly in England; but, in addition to the inconvenience exhibited by the papers so treated, the operation was delicate, expensive, and had to be performed on paper already in sheet form.

Attempts were then made to glaze the paper in the vat, and D'Arcet was the first to propose a practical formula for the use of vegetable glues. His mixture had the following composition:—

Starch	12 parts,
Resin (dissolved in half part of sodium carbonate)	1 part,
Water	315 parts,

these proportions being employed per 100 parts of dried pulp. The papers made in this manner were deficient in tenacity, and D'Arcet altered the formula to

Flanders glue	4 parts,
Resin soap	8 ,,
Alum	8 ,,

per 100 parts of dried pulp.

According to Payen, the resin soap is prepared by crushing and sifting 150 parts by weight of resin, which is then treated with a hot caustic lye obtained by mixing 75 parts of soda crystals, 375 parts of water, and 12 parts of lime. The amount of water is increased, by the washing water and the steam used for heating, to 150 parts, and, after boiling for half an hour, 750 parts of resin soap are obtained.

As this soap would not mix very easily with the pulp, 75 parts are dissolved in 500 parts of lukewarm water containing 20 parts of starch, the granules of which swell up considerably in the solution when raised to boiling temperature by a jet of steam.

This liquid is added to the pulp and, after about a quarter of an hour, is stirred up well and mixed with a solution of alum, which forms an insoluble impermeable glue. The following proportions are often employed:—To each cwt. of fine paper and 210 gallons of water are added about 82 gallons of agglutinant (prepared as above), and the whole is precipitated with 4½ lbs. of alum.

According to Planche, 210 parts of water, 16 parts of 80° soda, and 8 parts of lime, boiled for 3 or 4 hours, are required to dissolve 100 parts of resin. After leaving to clarify, the clear liquor is drawn off, and the caustic lye is run into soap-making pans. The resin is thrown in bit by bit, the mass being kept stirred and raised to boiling point until the whole is dissolved, which takes about 4 or 5 hours. In the earlier stage the heat must be applied with caution, in order to prevent the resin soap from boiling over. In order to use this soap without any addition of starch, a portion is then thinned down in 20 parts of hot water, the solution being left to settle for 1 or 2 hours, and afterwards drawn off as required. To mix starch with this, the soap solution is run off into a pan, and incorporated with starch, previously mixed with warm water and passed through a fine sieve. As soon as the mixture is complete it is boiled for half an hour, with continued stirring. Usually 2 parts of starch are taken to every 3 parts of resin.

When the pulp is well impregnated with the agglutinant it is precipitated by alum, as already stated. Liesching states that better results are obtained by adding alum first and the resin agglutinant afterwards, the alum apparently penetrating the pores of the paper in a more complete manner.

Aluminium sulphate may be advantageously used in place of alum, but should not contain any free acid. For white papers, or those to be coloured in light tints, the alum should not contain iron (P. Charpentier, article on " Paper" in Fremy's *Encyclopédie*). If the paper is to be blued with ultramarine, it is essential for the alum or the aluminium sulphate to be perfectly free from uncombined sulphuric acid.

Aluminium sulphate and alum are also employed in paper-making as mordants for fixing colours, just as in the dyeing industry.

137. **Application for hardening Plaster.**—It has long been known that plaster prepared with solutions of certain salts sets much harder than when mixed with water alone. The use of alum for this purpose was proposed by Pauware, the process being afterwards improved by Greenwood, and thoroughly investigated by Elsner (Knapp). In Pauware's original process the plaster articles were treated with alum solution after casting, by steeping them for a month in a solution consisting of 1 part of iron-free alum and 12 parts water at a temperature of 15 per cent. They were then washed and dried in a current of hot air. After this treatment the plaster was found to have increased in hardness and no longer soiled the fingers : at the same time, it could only be scratched with difficulty by the finger-nail; but after a time the articles proved incapable of resisting the influence of moisture, and, in addition, assumed an irregularly distributed greyish coloration. Moreover, plaster treated by this process softened to such a degree as to easily take the impress of finger-prints. In the second process the block plaster heated in the ordinary manner is plunged for several minutes into a solution containing 8 to 10 per cent. of alum, and is then calcined over again at a dark red heat; the temperature must be uniform and constant. The resulting plaster is dull, and has a milk-white colour, or faint Isabella tint; and can easily be reduced to powder. If the temperature in the second baking has been pushed too far, the

edges of the blocks are as hard as stone; they can only be powdered with difficulty, and are really scorched.

Articles manufactured of alumed plaster set much more slowly than those of ordinary plaster, but finally attain a degree of hardness resembling alabaster or marble; and, besides, exhibit at the edges and thinner places a kind of translucence which further increases this resemblance. Slabs of a certain thickness can only be broken with difficulty under the hammer, and when left exposed to the weather for several months they remain intact without loss of hardness. According to Elsner, this alumed plaster will stand immersion for several hours in boiling water without its resistance being appreciably impaired.

Different explanations have been advanced to account for the hardness of this plaster. Payen ascribed it to the formation of a double salt of lime and potash, the crystals of which are enveloped in a precipitate of alumina. Landrin, who examined several specimens of alumed plaster such as are used for stucco work in France and England, stated them all to be almost perfectly pure, free from alumina and potash, and well baked; and he was led to conclude that their slow rate of setting could only be ascribed to chemical reaction set up between the aluminium and potassium sulphates and the plaster, resulting in the conversion of all the calcium carbonate into sulphate.

According to this view, the action of the alum is entirely due to its sulphuric acid, and Landrin sought to verify this hypothesis by reacting on plaster with a number of soluble sulphates, such as those of sodium, potassium, ammonium, etc.

By restricting the additions to the quantity absolutely necessary to saturate the calcium carbonate, he obtained about the same results as with alum. He afterwards found that sulphuric acid by itself is able to play the same part, and was thus led to a simple and practical method of preparing alum or *stucco* plaster.

This process consists in steeping the raw plaster for about 15 minutes in water containing 8 to 10 per cent. of sulphuric acid, and then baking it in the ordinary manner. The stucco produced in this way is not only of the best quality, but also, thanks to the dissociation of a small excess of sulphuric acid, the organic matter always present to a small extent in gypsum, is burned away, so that the resulting plaster is of exceptional whiteness instead of being grey like ordinary stucco.

Care must, however, be taken to heat the plaster sufficiently to drive off all the free sulphuric acid, since the least trace of residual acid will alter the properties of the product by rendering it very hygroscopic; moreover, the fritting temperature of the plaster must not be exceeded. The best baking temperature lies between 600° and 700° C.

After having demonstrated that the effect of alum on plaster is solely due to the action of the sulphuric acid on the calcium carbonate therein, Landrin investigated the retardive influence of alum or sulphation on the setting of ordinary plaster, and put forward the following explanation:—

"If it be admitted," he says, "that by baking gypsum at a fairly high temperature the affinity of this body for water is partly removed, immediate combination between the sulphated plaster and water is prevented; and, the chemical action being very slow, the same will apply to the desiccation, and the setting will be delayed. It is not until afterwards, when the water has been partly dissipated into the atmosphere, that the solution can become supersaturated; and then only will the plaster set hard."

If this explanation be accurate, one ought to be able to cause the plaster to set at once by heating it gently when the water has been added; and this is precisely what does occur. The same result can be obtained by mixing slow-setting plaster with ordinary plaster, the latter commencing to set and imparting the same tendency to the rest of the mass. Again, by employing hot water in making the plaster, the more rapid evaporation of the liquid hastens the setting. Consequently the analogy between the phenomena of setting in ordinary and sulphated plaster is complete; the sole difference consists in the loss of chemical affinity produced by an excess of warmth—a difference that is found at a maximum in the case of anhydrite, which will not set with water at all (Knapp).

The alum plaster or stucco is chiefly employed for articles of indoor decoration, on account of its hardness when set and its resemblance to marble; a likeness that can be heightened by employing plaster of various shades to produce marbled effects. In such event recourse is had to pigments: minium, chrome yellow, colcothar, terra di Sienna, lampblack, etc., added to the water, mixed with glue, used in making the plaster. By placing several layers of differently coloured plaster one above another a mass of striped appearance in section can be obtained, which will imitate the aspect of marble when applied so as to expose portions of these different layers.

This class of stucco can also be polished.

138. **Application to Lime Washes.**—The extent to which lime washes are employed to coat the external surface of houses in country districts is well known; and the same preparations are also largely used for indoor work, particularly in stables, etc. In addition to being cheap and enabling the appearance of walls to be improved and their materials protected from the weather at a small outlay, this method also exhibits the advantage of disinfecting insanitary premises.

Lime wash, prepared by mixing fat lime and water, does not, however, adhere very well to the surfaces to which it is applied, and rapidly peels off. This inconvenience may be remedied by the addition of a little alum at the time of use, the precipitate of gelatinous alumina thus produced enveloping the particles of lime and helping them to stick. The coating of lime is then much more firm and durable than usual.

139. **Application to the Preparation of Non-inflammable Wood, Fabrics, etc.** — The extreme inflammability of the materials used in building has led to many disastrous fires—notably that at the Charity Bazaar in Paris not very long ago; and many fatalities could undoubtedly have been prevented had the fabrics and wood used in building been impregnated with some metallic solution to render them less inflammable and thereby prevent the rapid propagation of fire.

The use of alum for this purpose has often been recommended, and the author's personal experience speaks in favour of such a course, he having found that wood steeped for several hours in a hot solution of alum becomes perfectly incombustible after drying. And if we may give credence to the statements of ancient writers, this salt was used for the same purpose at remote periods, it being recorded by Aulus Gellius that, during the siege of Athens by Sylla, Archelaus constructed a wooden tower which could not be set on fire, the wood having been impregnated with alum.

140. **Application to Bleaching.**—A bleaching preparation, recommended by Orioli, is obtained by decomposing a solution of chloride of lime with aluminium sulphate. The product being very unstable, no acid is required. Its bleaching action is due to decomposition into aluminium chloride and oxygen.

141. **Application to Photography.**—Alum is the salt principally used in this connection.

After developing, the (gelatino-bromide) plate is well washed, and then immersed in a 5 per cent. alum bath, whereby the pellicle hardens and loses its tendency to detach or wrinkle. Plates that have turned yellow on exposure may be bleached by 5 minutes' immersion in a bath of

Water	1000 parts,
Alum	100 ,,
Hydrochloric acid	20 ,,

and can be then washed immediately and fixed.

The alum treatment is not indispensable, but is nevertheless useful in preserving the plates.

142. **Employment in Medicine.** — Here again alum is mainly used. Calcined, it is employed as a caustic; in the ordinary condition it serves for the preparation of certain gargles, etc.

143. **Application to the Purification of Waste Waters.**—The waste waters from various industries, sewage water, etc., contain larger or smaller quantities of fats, organic and mineral matters in solution or suspension, the more dangerous from a sanitary point of view being the organic substances, since they begin to putrefy after a while and contaminate the water-courses into which they are discharged. The necessity of chemically purifying these waste waters has long been recognised, and

aluminium sulphate is certainly one of the best agents to which recourse has been had for this purpose.

When this product is added in small quantity to an alkaline water, or one that has been rendered alkaline by lime, an abundant gelatinous precipitate forms and carries down with it all the matters present in suspension. This precipitate is aluminium hydrate, a body which, as we have already seen, has a great affinity for certain organic matters in solution and forms lakes with the same.

Aluminium sulphate has also been used for treating the liquids furnished by various processes for dealing with sewage. Thus in the Lencauchez process the liquids freed from ammonia and boiled with an excess of lime are delivered into decantation tanks, where they are treated with a small quantity of aluminium sulphate (about 1½ ozs. per cubic yard) to facilitate the deposition of suspended matters and hasten decantation.

In the Hennebutte and De Vauréal process the total sewage is treated with aluminium sulphate (5 parts per mil.) and zinc sulphate (2 to 3 parts per mil.), the mixture being left to settle and the clear liquid afterwards decanted off and sent to the ammonia recovery plant. The sediment is again treated with the same reagent, and is delivered, by the aid of compressed air, to a filter-press which furnishes firm cakes—easily dried by exposure to air—and a clear liquid which is added to that first obtained.

The addition of aluminium sulphate and zinc sulphate desulphurises the matters present, and the gelatinous alumina precipitate carries down the bodies held in suspension. The cakes obtained in this way contain, when dry, 3 to 4 per cent. of nitrogen and about 3 per cent. of phosphoric acid (C. Vincent).

Alum is very well adapted for use in purifying waste liquors, and may be obtained from the makers in a crude form, which is just as good for this purpose as the commercial grades and far less expensive. In use the alum crystals are put into a bag, which is then placed in the channel through which the liquors to be purified are discharged. The alum is thus gradually dissolved and mixed with the flowing liquid, the resulting precipitate of alumina carrying down the matters in suspension. The precipitate is collected in the settling tanks.

It is thus evident that the uses of alum and aluminium sulphate are both numerous and extensive.

CHAPTER VI

USES AND APPLICATIONS OF FERROUS SULPHATE AND FERRIC SULPHATES

§ I. USES OF FERROUS SULPHATE

144. **Ferrous Sulphate in Dyeing.**—*A.* AS A MORDANT.—Ferrous sulphate is known by the name of *green vitriol* and *green copperas*, and is prepared in the manner already described. Its uses as a mordant are somewhat limited.

(1) *On Cotton.*—Ferrous sulphate is generally used to dull the shades after dyeing. The cotton is boiled in a decoction of the dye stuff, the excess of liquor being eliminated and the cold ferrous sulphate solution then used. This method is only suitable for light tints. A better plan is to impregnate the cotton with a tannin principle and then immerse in ferrous sulphate solution: for this process, however, ferric sulphate is to be preferred.

Ferrous sulphate is used in the same manner as ferric nitrate for the production of chamois tints on cotton.

(2) *On Wool.*—For this purpose ferrous sulphate has been largely superseded by potassium bichromate, but is still used in certain cases.

Wool may be mordanted by boiling in a suitable mixture of ferrous sulphate and cream of tartar, a fairly large proportion of the latter being required.

In certain cases (sandal-wood, etc.) it is better to boil the wool first in a decoction of the dye until the greater portion of the latter has been absorbed, the ferrous sulphate being then added to the same liquor, or in a separate bath, in the proportions of 5 to 8 per cent. of the weight of wool taken, boiling being continued for ½ an hour or longer (Hummel and Dommer).

(3) *On Silk.*—Ferrous sulphate is not very much used in this particular case. It is employed as a mordant in paper staining.

B. APPLICATION TO THE MANUFACTURE OF OTHER IRON MORDANTS.—Ferrous sulphate may be utilised in making ferrous acetate, which is somewhat largely employed in dyeing and is prepared by double decomposition between ferrous sulphate and lead acetate or calcium acetate. The method of treating ferrous sulphate for the preparation of normal ferric sulphate or of *rouil* mordant has already been described.

C. APPLICATION TO INDIGO DYEING.—The principal method of indigo dyeing is based on the property of this pigment of undergoing conversion, under the influence of reducing agents, into indigo white—which is soluble in alkaline solutions, can be fixed on the fibre, and then under the oxidising influence of the air is transformed into insoluble indigotin firmly fixed on the fibres.

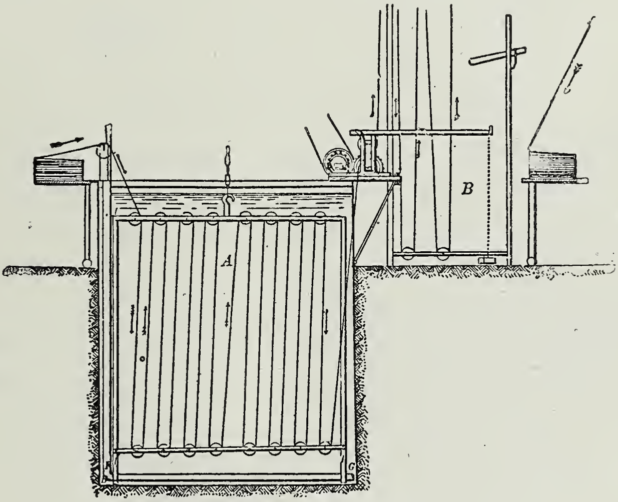

FIG. 185.—Indigo dyeing. Ferrous sulphate vat.

The vats used in indigo dyeing may be classed, according to the reducing agents employed, as ferrous sulphate vat, zinc vat, and hydro-sulphite vat. These vats are mainly used in cotton dyeing. Our attention is confined to the ferrous sulphate vat, or, as it is generally termed, the lime and copperas vat. These vessels are rectangular in shape, and are constructed of wood, stone, or cast-iron. The size varies according to the material to be dyed.

For calico dyeing the usual size is 40 × 40 × 20 inches; for hank dyeing they are made a little smaller. In order to economise the indigo, the vats are arranged in series.

The bath liquor for dyeing calico consists of—

Water	880 gallons,
Crushed indigo	88 lbs.
Ferrous sulphate	154 ,,
Quicklime	165 ,,

For yarn dyeing, proportions are—

Water	165 gallons,
Indigo	8·8 lbs.
Ferrous sulphate	15·4 ,,
Quicklime	17·6 ,,

The reactions in the bath are very simple:—lime reacts on the ferrous sulphate to form very unstable ferrous hydrate, which latter, in presence of indigo, reacts on the water and is converted into ferric hydrate, nascent hydrogen being liberated and immediately reducing the indigotin to indigo white. This latter then combines with the excess of lime and enters into solution.

The reaction may be expressed by the following equations:—

$$(1)\ FeSO_4 + CaO + H_2O = CaSO_4 + Fe(HO)_2,$$

$$(2)\ 2[Fe(HO)_2] + 2H_2O = Fe_2O_3,\ 3H_2O + H_2,$$

$$(3)\ C_{16}H_{10}N_2O_2 + H_2 = C_{16}H_{12}N_2O_2.$$

A freshly prepared vat can be considered in proper condition if the liquid, on being stirred, exhibits numerous deep blue veins at the surface, which is covered with a thick scum. The bath liquor should be clear and of an amber-brown colour.

It makes little difference in what order the various substances composing the bath are added, but it is highly necessary that the ferrous sulphate should be as pure as possible. An excess of this salt or of lime should be avoided.

At the end of the day's work the baths should be stirred up vigorously, and should receive slight additions of lime or ferrous sulphate according to their appearance.

Before dyeing, the scum should be taken off with a skimmer, to prevent it spotting the stuff or yarn.

This bath is mainly used for cotton. The fabric is first boiled in water to enable it to take the dye uniformly.

For dyeing pale blue, only a few hanks are treated at a time, and the operations must be conducted with the greatest regularity; but such great precaution is unnecessary when dyeing dark shades. The length of immersion varies from 1 to 5 minutes and more, according to the shade required; and after wringing the hanks they are set aside to oxidise completely.

The most economical plan is to dye systematically, the cotton being entered into the weakest baths first and afterwards into progressively stronger ones until the desired shade is attained. In this manner each bath becomes completely exhausted in turn. After dyeing, the lime deposited on the fibre is removed by a bath of sulphuric acid (density, 1·01 to 1·02). This operation removes the grey tinge and brightens the colour. A final washing is then given, but not too energetically, as otherwise the indigo may partly run and the shade will be deficient in uniformity and intensity.

For dyeing calico, the piece goods in a dry state are suspended on a square wooden frame and immersed in the bath for 15 to 20 minutes; they are then taken out of the bath and exposed to the air for a similar period. The continuous machine of the kind shown in Fig. 185 is often used for calico dyeing, the pieces being passed over a series of rollers mounted on wooden frames in the bath. On issuing from the bath the goods are passed between wringers and then over other rollers on the outside, where oxidation occurs, the operation being repeated several times according to the shade required. The pieces are then rinsed in pure water, then in dilute sulphuric acid, and are finally washed and dried (Hummel and Dommer).

145. **Application of Ferrous Sulphate to the Manufacture of Pigments.**—*A*. PRUSSIAN BLUE.—Prussian blue is a ferric ferrocyanide—

$$(Fe''Cy_6)_3, (Fe_2^{VI})_2 + 18H_2O = Fe_7Cy_{18} + 18H_2O.$$

It was discovered by accident as long ago as 1704, and was prepared at Berlin by Diesbach, a colour maker, and Dippel, a pharmacist, who kept their process a secret. The first process for making this pigment on a large scale was described by Woodward before the Royal Society of London in 1724.

Up to the present time the only known method of obtaining Prussian blue of good quality is by precipitating ferrous sulphate with ferrocyanide. The potassium ferrocyanide solution must be run by degrees into the slightly acidified ferrous sulphate liquor, the converse procedure being inadmissible owing to the retention, in that case, of a large proportion of ferrocyanide by the precipitate. Furthermore, the washing from the precipitate should be examined for traces of ferrocyanide (blue precipitate with ferric salts).

The best proportions are—

Ferrous sulphate	6 parts,
Potassium ferrocyanide	6 ,,

each dissolved in 15 parts of water.

After mixing, an addition is made of 1 part concentrated sulphuric acid and 24 parts fuming hydrochloric acid. This forms a white precipitate of ferropotassic ferrocyanide, which, on oxidation, furnishes Prussian blue—

$$6(\mathrm{FeCy_6.Fe''K_2})+3\mathrm{O}=\mathrm{Fe_7Cy_{18}}+3\mathrm{K_4FeCy_6}+\mathrm{Fe_2O_3}.$$

This precipitate can be oxidised either by contact with air or by the action of nitric acid, chromic anhydride, chlorine, bleaching chlorides, etc.

In the above-mentioned case a clarified solution of chloride of lime is added, by degrees, several hours after the addition of the sulphuric and hydrochloric acids. The precipitate is then left for several hours, and afterwards washed and dried. It is purified by digestion with hydrochloric acid followed by washing with water. It has been already stated that a certain quantity of alum is precipitated along with the ferrous sulphate in order to improve the quality of the blue; consequently this need not be further dilated upon.

B. MANUFACTURE OF MARS, OR MARTIAL, PIGMENTS.*—These pigments are artificial ochres of handsomer colour than the natural pigments they are used to replace.

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* So called from the ancient alchemical name of iron (namely Mars), *e.g.* martial pyrites.

(1) *Mars Yellow.*—This is prepared by treating a pure solution of ferrous sulphate with sufficient milk of lime to completely saturate the sulphuric acid. A precipitate of ferrous hydroxide intimately mixed with calcium sulphate is formed, and this is agitated in contact with air until the oxidation is complete. The product is a yellow ochre of very pure shade and highly transparent (Guignet).

When ammonia is used as a precipitant the product is darker and less pure in tone.

(2) *Mars Orange.*—This is obtained by moderately treating ferrous sulphate, the products being basic ferric sulphates varying in colour according to the temperature of calcination.

(3) *The Capuchin Reds, Flesh Colours, etc.* used in painting on porcelain may also be obtained in this manner. It is necessary to wash these products thoroughly in order to remove the soluble sulphuric acid.

(4) *Mars Violet* is obtained by calcining ferrous sulphate at a very high temperature. The pigment is very hard to grind, and is somewhat dull, though very durable (Guignet).

C. Colcothar.—This residue is obtained on decomposing ferrous sulphate by heat in the manufacture of fuming (Nordhausen) sulphuric acid. It should be washed with great care in order to remove all traces of sulphuric acid. The shade obtained varies according to the calcination temperature employed.

146. **Application to the Manufacture of Writing Inks.**—A large number of recipes have been put forward for the preparation of writing ink. This ink has a basis of iron tannate, and entails the use of three principal materials, namely *gall nuts*, *gum*, and *ferrous sulphate.*

The gall nuts (of the best quality) are crushed, 1 part of the product being infused for 24 hours in 14 parts of pure (preferably distilled) water. It is then boiled for half an hour and filtered through a cloth.

On the other hand, $\frac{1}{2}$ part of gum arabic or Senegal gum is dissolved in 1 part of pure lukewarm water and added to the decoction of gall nuts.

Finally, $\frac{1}{2}$ part of pure ferrous sulphate is dissolved in 1 part of hot water, filtered, and run by degrees, with continued stirring, into the previous mixture.

This ink turns very dark in time, but afterwards gradually loses its colour and assumes a yellow tinge. Ink made from gall nuts rapidly becomes infested with mould fungi, a defect which can be corrected by a small addition of phenic acid or salicylic acid.

To convert this ink into copying ink, it is merely necessary to add a little sugar and glycerin.

147. **Employment in Microbiology; Staining the Cilia of Bacteria.**—The vibratory cilia of the motile bacteria are difficult to stain, and special methods have to be employed in order to facilitate their examination. One of the best methods is that of Lœffler. When dried and fixed, the plates are subjected to the action of a mordant bath composed as follows:—

Cold saturated aqueous solution of ferrous sulphate . .	5 c.c.
Aqueous solution of tannin (20 grms. to 80 grms. of water) .	10 ,,
Saturated solution of fuchsine in absolute alcohol . .	1 ,,

They are then stained with a saturated solution of fuchsine in aniline water.

148. **Application to Photography.**—Ferrous sulphate has been largely used in photography as a developer. On the one hand, a solution is made of—

(1) Potassium oxalate	250 grms.
Water	1000 ,,

and another of—

(2) Ferrous sulphate	100 grms.
Water	300 ,,
Sulphuric acid	5 drops.

Solution No. 1 is stable and will keep indefinitely, but No. 2 solution oxidises in the air, and should only be prepared in small quantities at a time.

For use, the ferrous sulphate solution is poured into the oxalate solution and the plate is developed in the resulting bath. It is advisable to add the ferrous solution in small quantities at a time, and according to requirement, as revealed by the progress in developing. For example, 80 c.c. of the oxalate solution are measured into the dish, 25 c.c. of ferrous solution being measured out, but only ⅓ added at first. The plate is then immersed, and, according to the way the image comes up, the second or even third portion of the solution is added afterwards.

149. **Application to the Manufacture of Nordhausen Sulphuric Acid.**—This process will be dealt with in treating of ferric sulphate, the raw material employed being a mixture of ferrous sulphate, ferric sulphate, and aluminium sulphate obtained by treating shale.

150. **Application of Ferrous Sulphate for Disinfection.**—Ferrous sulphate is, with justice, largely employed for disinfection. It is precipitated by ammoniacal and sulphide products, which are thereby fixed. For example, with ammonium sulphide the following reaction occurs:—

$$FeSO_4 + (NH_4)_2S = (NH_4)_2SO_4 + FeS.$$

It is also used in domestic hygiene for disinfecting cesspools, etc., several pounds of the salt being thrown in at intervals. Again, it is employed for treating waste waters and sewage in the manufacture of ammonia salts and fertiliser cakes, its action being to destroy the sulphides and fix ammonia.

Ferrous sulphate has likewise been utilised for disinfecting mud, street sweepings, and other decomposing material likely to prove injurious to the public health.

Rabot's method has proved satisfactory wherever tried. It consists in steeping the matters to be treated with a saturated solution of ferrous sulphate at the rate of 1 lb. per cubic yard, and then covering them with double that quantity of milk of lime. This method was adopted during the cleaning out of the Versailles Canal and the lake at St. Mandé.

151. **Application in the Metallurgy of Gold.**—This application is based on the precipitation of gold, in the metallic state, by a solution of ferrous sulphate, a reaction also utilised in analysis. The auriferous mineral is roasted and chlorinated, the gold being converted into a soluble chloride. The mass is then extracted, and the yellow liquor is treated with ferrous sulphate solution. After several hours' repose the clear liquor is drawn off and the muddy precipitate of metallic gold is collected.

152. **Application to the Purification of Lighting Gas.**—The necessity for chemically purifying lighting gas has been apparent ever since it began to be made; and as soon as the gas leaves the scrubbers it is treated to remove the tar. There, nevertheless, always remains a certain quantity of injurious or malodorous gases, which cannot be got rid of except by chemical reagents. These impurities comprise H_2S; CO_2; SO_2; CN; HCNS; CS_2; NH_3; etc.

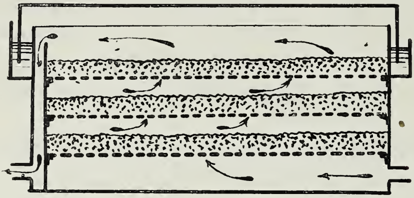


Fig. 186.—Laming purifier. Original form.

At first the gas was simply passed over slaked lime; but as this gave but a very deficient purification, metallic solutions were afterwards tried, ferrous sulphate in particular. As the purification still remained incomplete, and inconvenience arose through the pressure produced in passing the gas through the liquid, further attempts were made, and finally the reagent known as Laming's was prepared, in which ferrous sulphate plays a principal

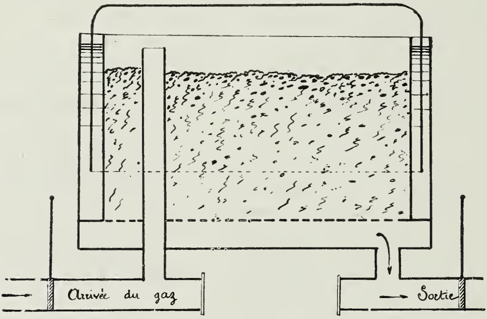


Fig. 187.—Laming purifier. Present form.
Arrivée du gaz = gas inlet; Sortie = gas outlet.

part. This is in the form of a powder containing ferrous sulphate, calcium hydroxide, slaked lime, and sawdust, the first-named being dissolved, mixed with the slaked lime, and the product thrown up into heaps in admixture with the sawdust.

The following reaction occurs:—

$$FeSO_4 + Ca(HO)_2 = CaSO_4 + Fe(HO)_2.$$

The mixture thus containing at first, $Fe(HO)_2$, $CaSO_4$, $Ca(HO)_2$ in excess, and sawdust. By exposure to air, the ferrous hydroxide is converted into $Fe_2(HO)_6$. Equal proportions of the ingredients are taken to form the mixture, the result being that the quicklime is in excess.

This mixture is placed in the purifiers, which at one time were made in the shape of boxes containing several layers of trays charged with the mixture, intermediate spaces being left for the circulation of the gas (Fig. 186).

At the present time the Laming mixture is used in the form of a single layer 20 to 40 inches in thickness.

The apparatus consists of a large sheet-iron tank (Fig. 187), 12 to 24 feet square, set on the ground and provided with a gas-inlet pipe projecting from below nearly to the top; another pipe, leading from the bottom, serving to draw the gas away. The mixture is placed on a perforated false bottom fixed at a certain distance from the real bottom of the tank.

The purifiers are arranged in sets, generally four, three of them being always in use. The operation should be carried on systematically, a system of pipes being provided so that each purifier can be put in communication with any of the others in the set. The arrangement is very simple, all the pipes leading to or from the purifiers opening into a central tank filled with water and containing a bell divided into compartments—as shown in diagram, Fig. 188—the central one receiving the gas from the

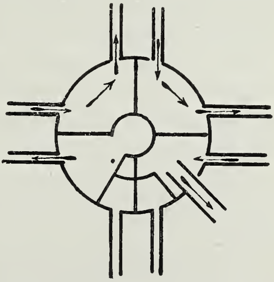


FIG. 188.—Distributor bell for a set of Laming purifiers.

scrubbers. To change the direction it is only necessary to turn the bell round through an angle of 45°.

The first stage of the action of the Laming mixture is the absorption of CO_2 by the lime, $CaCO_3$ being formed. The H_2S is readily absorbed by the $Fe_2(HO)_6$, according to the equation

$$2Fe_2(HO)_6 + 2H_2S = 2Fe(HO)_2 + S_2 + 4H_2O.$$

The lime also absorbs the SO_2 present; and, in addition, forms $Ca(CN)_2$ with the cyanogen, and $Ca(CNS)_2$ with the HCNS.

CS_2 is sparingly absorbed by the lime, but is taken up by calcium sulphide, whereas a little H_2S is always fixed by the lime—

$$CaO + H_2S = CaS + H_2O,$$
$$CaS + CS_2 = CaCS_3,$$

calcium sulphocarbonate being formed.

The ammonia is mainly in the form of carbonate, which, in presence of $CaSO_4$, gives $CaCO_3$ and $(NH_4)_2SO_4$.

The gas is thus purified, but at the end of a certain time the Laming mixture ceases to act, its composition then being a mixture of $CaCO_3$, $Fe(HO)_2$, S, $Ca(CN)_2$, $Ca(CNS)_2$, CaS, $CaCS_3$, $(NH_4)_2SO_4$.

It may, however, be regenerated, for which purpose it is taken out of the purifiers, mixed with a little slaked lime, and exposed to the air, whereby the $Fe(HO)_2$ is re-converted into $Fe_2(HO)_6$, and the mass is ready for use over again. After a certain number of times the mixture gets into such a condition as to be incapable of further regeneration, and must then be replaced by a fresh batch.

The spent mass, which contains 30 to 45 per cent. of sulphur, ammonia salts, and cyanides, is treated for the recovery of these bodies.

153. **The Uses of Ferrous Sulphate in Agriculture** are very numerous, and many of them highly interesting. The chief of these will now be discussed, special mention being made of one of the most recent, but most original, namely, the destruction of wild mustard or charlock (*sinapis arvense*) in cultivated crops by solutions of ferrous sulphate.

A. DESTRUCTION OF MOSS IN PASTURE LAND.—Damp pastures are generally infested with moss, which hinders the growth of grass and reduces the quantity and quality of the forage. To destroy this moss, successful experiments have been made by dressing the surface with about 300 to 500 lbs. of powdered ferrous sulphate per acre, applied by hand or in a drill. The work is generally performed in the early spring, in damp weather, before vegetation re-commences. February and March are also suitable months.

A still more effectual method is to water the pasture with a 5 to 10 per cent. solution of the ferrous sulphate.

In about 8 or 10 days the moss turns quite black, and should then be broken up (by cross-harrowing, etc.), gathered in heaps and carted away. Should the first treatment prove insufficient, the work should be repeated without hesitation.

B. DESTRUCTION OF DODDER IN FODDER CROPS.—Ferrous sulphate has yielded certain results in this case. The clover or lucerne attacked by the parasite is mown close and watered with ferrous sulphate solution, a 2 per cent. solution being sufficient if applied as soon as the parasite appears; but if left later, the strength must be increased to 3 to 4 per cent.

C. EMPLOYMENT IN TREATING CHLOROSIS, ANTHRACNOSE, ETC., IN VINES AND FRUIT TREES.—The distinctive signs of chlorosis in vines and other plants are well known, and consist in stoppage of growth, the leaves turning yellow, the twigs remaining thin and the plant stunted and barren. The causes are still somewhat obscure. In some cases the disease has been traced to poverty and lack of aëration of the soil; but generally it is attributed to an excess of lime. Some plants are more susceptible than others, but nevertheless the amount of damage done to the vineyards by this complaint was very great until Rassiguier discovered a simple and practical method of coping with it,—the means now generally employed and involving, in the aggregate, the consumption of enormous quantities of ferrous sulphate.

Rassiguier's method is perhaps best described in the words of his contribution to the *Bulletin de la Société des Agriculteurs de*

France (1st January 1896) on the treatment of chlorosis in vines by washing with ferrous sulphate :—

"The treatment with ferrous sulphate, as an antidote to chlorosis, which I invented in 1891 and tried on my own property, has furnished such results that the method has spread, and experience has taught its value to both scientists and practical wine-growers.

"For the benefit of those who are still unacquainted with the details of the matter, I will briefly review the conditions to be followed as to the time, method of operating, and quantity of dressing to apply; and recount the influence of a single annual washing on chlorosis, anthracnose and 'short node' (*court noué*) in vines, fruit trees, and roses.

"To produce the full effect, washing should be performed in autumn, the vines most afflicted with chlorosis being treated first, as soon as the first leaves begin to fall; in fact, I think that such as are very much stunted should be treated before any of the leaves come off. Both are washed *immediately after each stock has been pruned.*

"All the wounds made in pruning should, *without exception*, be drenched with the ferruginous solution; and, in order to ensure the curing of the disease, the drenching should extend over the whole surface of the trimmed shoots (not excepting the buds, these being sufficiently protected by their downy envelope), the branches, and even the stem, as will be explained below.

"There is no need to be afraid of a more or less deep coloration of the trimmed shoots, and if any of these—insufficiently ripened, and therefore liable to perish—should succumb to the washing process their place will shortly afterwards be found taken by vigorous buds—beside or below the dead shoots—which will bear fruit the next year. All vines, well or diseased, may be washed with advantage, as the treatment strengthens growth.

"If postponed until the cold weather sets in, the washing will have little effect, and spring washing is less efficacious against chlorosis than autumn washing.

"An active woman, armed with a wooden pail and a brush —or, better still, a woollen rag tied up in the shape of a brush—

can wash after three pruners. During use the liquid should be stirred up at intervals to keep it fairly uniform in density. The solution should be a saturated one, *i.e.* containing 40 to 45 per cent. of ferrous sulphate, and may be prepared in a very simple manner by placing 80 to 90 lbs. of ferrous sulphate in a wicker basket slung on a stick through the handle, and thus suspended in a vessel large enough to hold 200 gallons of water without overflowing when the basket is immersed. After leaving over night the sulphate will be dissolved and the liquor ready for use by next day.

" Generally the results of the treatment are remarkably beneficial, and in many places a complete cure is effected the first year. However, some soils are less favourable to viticulture and require the treatment to be repeated. Chlorosis has also been cured in fruit and rose trees by washing the pruned surfaces with the same solution.

" Moreover, when the dressing is applied over the entire surface of the stock, it is capable of destroying the germs of oïdium, anthracnose, mildew, and insects lodged in the interstices of the bark.

" Three years' consecutive treatment of my own vines cured the stocks suffering from short node, *i.e.* those where the nodes on the sickly branches were only a few centimetres apart. These formerly unproductive stocks now yield a large crop, and the internodes are of ordinary length.

" First year's grafts may be treated with a 20 to 30 per cent. solution, the full dose being repeated the third or fourth year.

" Thus all the foregoing maladies are curable by a single annual operation.

" I recommend the pruner to cut through the middle of the bud just above the one destined to bear fruit, so as to leave intact the protecting septum existing at this point, and which, when cauterised at the surface by the action of the ferrous sulphate, preserves the adjacent internode from the effects of frost, insects, or wet, which might otherwise penetrate the pith: this internode remaining healthy, the fruit bud will be rendered more vigorous."

The importance and value of this method is confirmed by the report drawn up by M. Guillon (teacher of Viticulture at the National Agricultural School, Montpellier) on the experiments instigated by the Hérault Agricultural Society with reference to the treatment of chlorosis.

"1. At present, without taking into consideration the lime-resisting properties of the grape stocks, the best and most efficacious preventive against chlorosis of the vine is a thorough washing of the stocks with ferrous sulphate by the Rassiguier process.

"2. Ammoniacal iron citrate also restores stocks afflicted with chlorosis; but in addition to the fact that the action of this salt is unknown in the case of certain maladies curable by ferrous sulphate it is much too dear for its employment to be advocated.

"3. The best results ensue when the washing is performed at the time the leaves are beginning to fall, *i.e.* end October to early November in the south. Spring washing produces less decided results.

"4. The application of ferrous sulphate to the pruning cuts alone is nearly as efficacious as when the whole stock is dressed, which shows the importance of not neglecting these cuts when applying the dressing.

"5. The ferrous sulphate solution should be of 40 to 50 per cent. strength.

"6. In vines badly afflicted with chlorosis the remedy is not always completely successful the first year, and, even if apparently so, it is advisable to repeat the process for several seasons."

The action of ferrous sulphate in the treatment of chlorosis is somewhat difficult to explain. According to Coste-Floret, however—

"The buds and wood still continue to grow after the leaves have fallen; and the only way in which the plant can now procure the carbon dioxide necessary to its growth—which though small is continuous—is by decomposing the carbonates in the sap, and it is at this moment that the accumulation of lime salts increases in the young wood to such an extent as to endanger the previous year's growth. This being so, the Rassiguier process is readily explained, namely, the ferrous sulphate acts by paralysing the cells still active at the end of the season, and, by retarding this slow continuous vegetation subsequent to the fall of the leaf, it prevents the gradual and dangerous accumulation of lime salts in the plant. This is the reason why the process is not thoroughly efficacious except when applied immediately the leaves have fallen, because later on the mischief will have been already done."

Sahut recommends the following formula as a preventive against *anthracnose* :—

Ferrous sulphate	20 parts,
Copper ,,	12 ,,
Fat lime	6 ,,
Water	100 ,,

Ferrous sulphate has also been recommended as a remedy against fruit dropping off, when due to mildew. Coudercq found the best results were obtained by spraying during the winter with a solution containing 3 per cent. of ferrous sulphate and 5 per cent. of copper sulphate, or the latter salt by itself.

At the beginning of winter, and again in January, it is well to wash the trunks and branches of fruit trees with a 20 per cent. solution of ferrous sulphate in order to destroy insects and their eggs, flies, and moss.

As a remedy for canker, Prillieux advises excision of the diseased portions and washing with a 10 per cent. solution of ferrous sulphate. It is also well to scatter about 2 pounds of the powdered salt about the foot of each tree, for a distance varying with the size of the trees.

Ferrous sulphate has also been used as an insecticide, and employed, with more or less success, against aphides, caterpillars, etc. Again, G. Croquevieille recommends it for treating oïdium, mildew, black rot, etc. in the vine, and ergot, anthracnose, caries, etc. in cereals; but, in the author's opinion, it is pushing matters to extremes to claim universal curative powers for ferrous sulphate, as such a course will probably only lead to disappointment in a number of cases.

D. Destruction of Cruciferous Weeds.—These chiefly belong to the *Raphanus* and *Sinapis* species; the first-named, which is rare, being represented by only a single variety, namely the wild radish (*Raphanus Raphanistrum*, L.), a plant 4 to 8 inches in height, bearing white blossoms veined with brown or violet, and an elongated fruit which divides, when ripe, into portions containing only a single seed each.

The mustard tribe is more general, three varieties being found, namely white (*Sinapis alba*), black (*Sinapis nigra*), and wild mustard (*Sinapis arvense*), all of which bear yellow flowers, and vary in height from 8 to 48 inches.

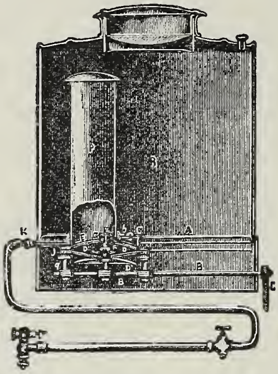


Fig. 189.—Portable spraying apparatus.

R, Receiver; A, bottom wall traversed by the pump P; D, circular rubber diaphragm acting as piston; J, metallic joint supporting D; E, piston rod connected to the diaphragm by two convex discs D^1, and actuated from the shaft B; C, handle for working the shaft B and pump; *b*, *b*, apertures admitting liquid to the pump, and closed by discs during the compression of the diaphragm; I, orifice admitting the liquid in the pump to the air chamber in P, closed during the back stroke of the diaphragm; K, discharge pipe.

Apart from these types there are numerous hybrids of variable height and ramification, with yellow flowers more or less bright in colour.

All these plants produce large quantities of seeds that germinate readily. In some years they invade cereal crops so rapidly, and their growth is so luxuriant, that the wheat, oats, etc. are stifled and killed, or at any rate greatly enfeebled, the great loss caused by these weeds making them greatly dreaded by the farmer.

Weeding being a very expensive task, other means of eradicating these pests have been sought. Topping is the one generally pursued, but this is attended by the disadvantage of leaving the bulk of the plant intact; consequently the recent discovery of a rapid, simple, and cheap method of totally destroying the weeds was readily welcomed by farmers.

Copper sulphate was first used, in the condition of a 5 per cent. solution, applied, at the rate of 100 to 150 gallons per acre of the infested area, by a spraying engine similar to those generally used for copper solutions. This liquor destroys the cruciferous weeds, and leaves the cereal plants intact, their glaucous surface, with its thin overlying layer of fat, preventing them from being wetted by liquids. The copper solution therefore merely runs down the leaves of the cereals and falls to the ground without doing them any injury. On the other hand, the leaves, stems, and flowers of the cruciferous weeds are unprotected in the described manner, and consequently the copper solution adheres to their surface and acts as a caustic poison. A couple of days after spraying, the weeds look as though scorched, turn yellow, and commence to shrivel up; and in about a fortnight they will have entirely disappeared, leaving the cereals growing with vigour.

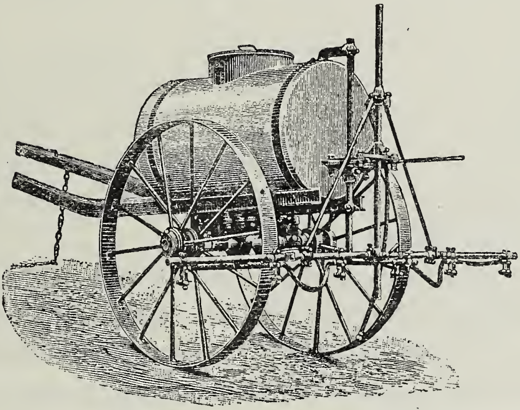


FIG. 190.—Spraying engine.

Copper sulphate being dear, especially for small consumers, who buy only a little at a time, a cheap substitute was sought in ferrous sulphate. True, a stronger solution (15 to 20 per cent.) of the latter is required to produce the same effect with the above-named volume of dressing per acre; but the treatment is thoroughly effective, and, in view of the lower price of ferrous sulphate, is less expensive than the copper sulphate method. The action of the two salts is not quite the same, ferrous sulphate acting mainly as a caustic, being transformed into a strong oxidising agent, ferric sulphate, in the tissues of the impregnated plants.

The difference in action is shown by the appearance of magnified sections of treated plants. Thus with copper sulphate there is hardly any exterior zone of dissociation, the epidermis remaining just as distinct as if no treatment had taken place. Only the cell contents have been altered, the protoplasm having contracted and adhered to the cell walls, although the section be taken from a still green undried plant.

On the other hand, with ferrous sulphate, besides the coagulation of the protoplasm, there appears around the edge of the section—where the plant has come in contact with the solution—a brown zone wherein the detailed structure is no longer perceptible. This zone has a scorched look, and extends more or less towards the centre.

In any event, the weed is destroyed—the main thing—this having been placed beyond doubt by the experiments made by the author and M. Vivien of St. Quentin. Other weeds, such as thistles, camomile, though rather more resistant, are also destroyed or greatly damaged.

The treatment should be applied when the cruciferæ have put forth their first leaves, though good results are still obtained during the flowering time.

This is a very important application of ferrous sulphate.

E. PRESERVATION OF STALL MANURE.—It has been proposed to employ ferrous sulphate to fix the ammonia in stall manure, and thus prevent the losses always occurring in manure heaps. Theoretically this should act all right, but in practice the result is the formation of a mixture of excrement and litter, which does not constitute stall manure.

F. FERROUS SULPHATE AS A FERTILISER.—Iron, in various stages of oxidation, is found in most arable soils, and is the cause of their brown or reddish colour. It is also found, though in very small proportion, in the ash of most cultivated plants; the following table, compiled by P. Gontier, showing the weight of ferric oxide per acre removed from the soil by different crops:—

Name of Plant.	Weight of Crop.	Weight of Ferric Oxide removed by Crop.
	lbs.	lbs.
Wheat (grain)	2500	0·200
,, (straw)	6000	9·900
Bere (grain)	3300	0·500
,, (straw)	6800	2·500
Barley (grain)	1850	0·700
,, (straw)	3000	3·400
Oats (grain)	1800	0·200
,, (straw)	3600	4·100
Sarrazin (grain)	1500	0·500
Maize (grain)	2800	0·300
Beans (grain).	2200	0·200
,, (haulm)	2200	0·400
Peas (grain)	1025	nil
,, (haulm)	2900	1·600
Vetches (seeds)	1040	nil
,, (haulm)	2900	0·900
Colza (seeds)	1505	0·200
,, (stems)	4500	4·000

An examination of the table shows that the iron is localised rather in the herbaceous parts than in the seeds. Nevertheless, it is none the less of great utility in plant life, as was shown by the labours of E. Gris in 1840, Knop in 1859, Dr. Sachs in 1860, and Boussingault in 1872.

The part played by this substance in vegetation has been mainly established by the researches of Dr. Griffiths, who carried out a large number of culture experiments with iron sulphate and phosphate, from which he drew the conclusion that not only do ferruginous manures increase the yield of most crops, but that they also exert manifest influence on the quality, particularly as concerns the increase of the albuminoids, carbohydrates, and fats, at the expense of water and fibre. Two examples referring to potatoes and beet are given below.

It results from experiments made by the same author that ferruginous manures in excess have an unfavourable influence on vegetation, and even a decided sterilising action.

The classes of soil requiring iron are, in the first place, all such as are deficient in organic matter, since, even if these soils contain sufficient quantities of iron, the latter would probably be inassimilable; secondly, siliceous soils containing iron in the condition of sparingly assimilable silicate; and thirdly, calcareous soils.

	Beet.		Potatoes.	
	With Ferrous Sulphate.	Without Ferrous Sulphate.	With Ferrous Sulphate.	Without Ferrous Sulphate.
Albuminoids .	2·89	1·90	3·92	2·24
Carbohydrates .	11·21	9·32	24·00	21·37
Fibrous materials .	1·98	2·05	1·61	1·00
Fatty bodies . .	0·25	0·21	0·29	0·21
Ash	1·52	1·00	1·50	1·21
Moisture . .	82·15	85·52	68·68	73·97
Total . .	100·00	100·00	100·00	100·00

For manurial purposes iron may be employed in the form of a compost of lime and ferrous sulphate, previously oxidised by aëration. To prepare this compost, the ferrous sulphate is dissolved in water, and the lime is added in powder, 1 part of slaked lime being taken to 2 parts of ferrous sulphate.

The dissolved salt is converted into an ochreous pulp, with which the remainder of the lime is then mixed. Ferrous sulphate may be also used by itself, in quantities from 50 to 200 lbs. per acre, according to the class of soil: for sandy soils from 50 to 100 lbs. is advisable, but for calcareous soils a larger quantity may be taken. Uniform distribution being desirable, it is a good plan to mix the fertiliser with soil or sand previous to sowing.

The dressing should be applied in the autumn, preferably on a warm day, immediately after rain; in default of rain, the best plan is to work after a good watering or on a dull day, the dressing being applied in nearly equal portions.

Great importance is attached to the conditions in which the ferrous sulphate is applied, and lack of care in this respect may lead to failure. A negative result will certainly follow if the salt be not sufficiently pulverised, if it be applied in dry weather, or if the temperature be too low, E. Grieg having found in his experiments that no effect ensues when the temperature is below 10° C. (A. Larbalétrier).

Ferrous sulphate is very frequently used in admixture with other substances, as a compound manure for pot and ornamental plants in the garden or the house. For foliage plants the following mixture may be used :—

Sodium nitrate	3 parts,
Superphosphate	4 ,,
Potassium chloride	1 part,
Calcium sulphate	4 parts,
Ferrous sulphate	2 ,,

applied at the rate of about 10 ozs. per square yard.

For flowering plants the proportions are as follows :—

Sodium nitrate	2 parts,
Superphosphate	10 ,,
Potassium chloride	2 ,,
Calcium sulphate	4 ,,
Ferrous sulphate	2 ,,

applied at the same rate as above.

§ 2. APPLICATIONS OF FERRIC SULPHATE

154. **Dyeing.**—*A.* COTTON DYEING.—Normal ferric sulphate is but very little used in cotton dyeing, the principal mordant employed, particularly for dyeing blacks, being the basic sulphate (*rouil*), the preparation of which has already been described.

The fabric is first entered in a cold bath of tannin material, and is then, or after passage through lime water, immersed for an hour in a bath of iron mordant diluted to a density of 1·01 to 1·02. The material is then washed, either in ordinary water or in water rendered alkaline by powdered chalk, in order to complete the precipitation of the basic salt on the fibre and to remove all traces of acid. The cotton is then dyed in a bath of campeachy.

In this operation the tannic acid, which is attracted by the cotton, mainly serves to fix the iron mordant, although incidentally it produces a bluish-black (inky) colour by combining with the ferric salt.

The passage through milk of lime after the tannin bath evidently causes the formation of calcium tannate, and the lime by taking part in the reaction facilitates the decomposition of the ferric salt.

This iron mordant may also be employed for dyeing chamois iron colours, for which the normal sulphate is still used (Hummel and Dommer).

B. WOOL DYEING.—Ferric sulphates are not generally used for mordanting wool, although they might be if properly applied.

C. SILK DYEING.—In this, again, the basic sulphate (*rouil*) is the most frequently used, the silk being mordanted in the condition of *grège* or as boiled silk. To mordant *grège*, the silk is first entered in a lukewarm bath (40° to 50° C.) of sodium carbonate. It is then washed, wrung, and entered into a cold solution of the mordant, diluted to a density of 1·075°, where it is worked for 30 minutes to an hour, then drained, wrung, washed, wrung again and worked for ½ an hour in a lukewarm bath of Na_2CO_3, followed by wringing and washing. These operations are repeated 3 or 4 times according to the object in view.

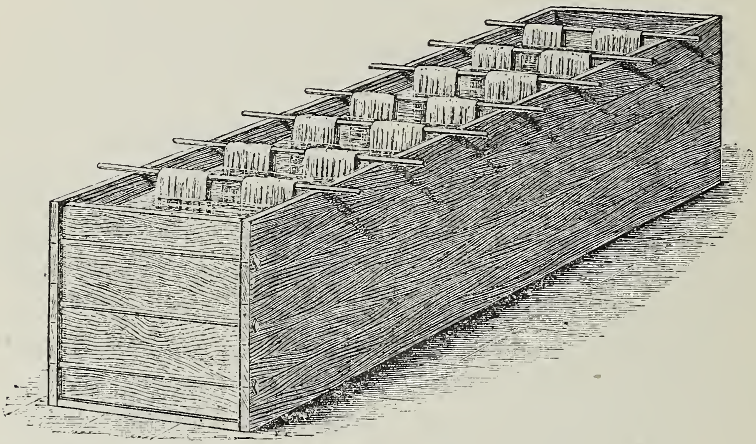


FIG. 191.—Mordanting silk.

For boiled silk the material is worked for 30 to 60 minutes in a solution of the mordant (density, 1·25). After rinsing it is washed, first in cold water, then in hot. These operations are repeated 7 or 8 times, the silk is afterwards boiled in an old soap bath, the soap used being generally the same as employed for boiling the silk, *plus* the addition of 12 parts of soft (olein) soap and 2 parts of soda crystals per 100 parts of silk. This soaping is continued at 100° for an hour in order to obtain a maximum fixing effect.

The mordanting is completed by a final washing. It being essential that silk mordanted with *rouil* should not be allowed to dry, the material must either be left in the mordant or else covered with damp cloths after washing.

Silk impregnated with ferric oxide gradually perishes if left in that condition, owing to the slow oxidation of the fibre. The differences in the method of fixing *rouil* mordant in these two kinds of silk are theoretical as well as practicable.

In the case of *grège* silk, for which a comparatively weak solution of mordant is employed, the *grège* itself causes the decomposition and precipitation of an insoluble basic salt within its own mass, fixation being completed by the washing and the rinsing in Na_2CO_3.

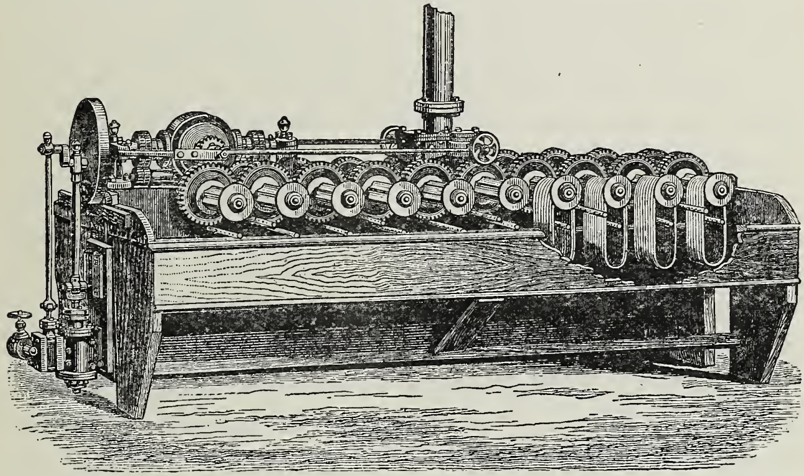


FIG. 192.—Washer employed for silk.

In the case of boiled silk, the fibre merely absorbs the mordant solution, and there is no decomposition or precipitation of basic salt until the solution is diluted by washing. The use of water containing calcium bicarbonate facilitates the fixing of the absorbed mordant, and the operation is completed by boiling in a soap bath.

Mordanted in this manner, the silk has a deep orange-brown colour and an improved lustre. The weight is increased 4 per cent. by a single mordant and 25 per cent. after six operations. After seven or eight repetitions there is a gain of about 8 per cent. on the original weight of *grège* silk.

The apparatus employed for mordanting silks is very simple, and consists of a rectangular vat to hold the mordant, the silk being hung on rods which are worked by hand in the bath (Fig. 191). After draining, the excess of liquid is removed by passing the hanks through a wringing machine.

For washing, the machine shown in Fig. 192 is employed. This contains a double row of glazed, fluted porcelain bobbins on which the hanks of silk are suspended and worked. The washing is effected by means of perforated pipes placed laterally underneath and between the bobbins (Hummel and Dommer).

D. USES OF FERRIC NITRO-SULPHATES.—These mordants are known as nitrates of iron, and are prepared by oxidising ferrous sulphate with nitric acid, which entirely or partly replaces the sulphuric acid. Their principal application is in dyeing cotton black, and they are used in the same manner as the ferric sulphates.

E. APPLICATION OF IRON ALUM, $Fe_2(SO_4)_3$, K_2SO_4, $24H_2O$. —This salt may be employed in the same manner as ordinary alum. Up to the present it has not been very largely used, its sole application being for mordanting wool previous to dyeing with alizarine colours (Hummel and Dommer).

155. **Ferric Sulphate as a Disinfectant and Antiseptic.**—*A*. INTRODUCTION.—The utilisation of the disinfectant and antiseptic properties of ferric sulphate forms one of the most important applications of this salt. The matter was investigated some twenty years back by Rohart, but we are indebted to Messrs. Buisine, of Lille, for the main of our knowledge on the subject; these last-named workers having devised the already described method of preparing the salt, namely that pursued in the Kuhlmann works at Lille.

Ferric sulphate forms with animal organic matter certain insoluble, non-putrefactive compounds of high stability, which are precipitated from solution and protected from subsequent decomposition under the action of air.

Urea, uric acid, mucus, gelatin, and albuminoids—in fact, all nitrogenous organic matters—are precipitated as non-putrefactive compounds.

When treated with ferric sulphate, fresh urine gives a precipitate containing nearly all the nitrogen and phosphoric acid, and the clear liquid will keep for a very long time without decomposing.

Human egesta, solid and liquid, can be preserved free from any trace of fermentation or liberation of gas by treatment with this reagent.

Animal remains, viscera, etc., will keep unchanged if immersed for some days in a 1 per cent. solution of ferric sulphate, and then washed and dried in the air.

In the same manner, small animals can be mummified whole, the flesh preserving its colour but being hardened to such a degree that it can with difficulty be scraped with the finger-nail. In fact, in the presence of animal matters, ferric sulphate behaves exactly like tannin and prevents putrefaction.

The foregoing results show the extent to which ferric sulphate modifies the character of organic substances, and the energy with which it retards or opposes putrefactive fermentation—in fact, the whole of its value as an antiseptic.

Its disinfectant properties are also easily explained. The action of ferric sulphate on solid organic matter has just been described; and this action is equally complete in the case of organic matters in solution, *e.g.* albuminoids, these being precipitated in the form of unalterable, non-putrefactive compounds of ferric oxide. Moreover, in the case of liquids on the way to putrefaction, ferric sulphate eliminates the decomposition products, especially sulphuretted hydrogen, ammonia, etc., the former being thrown down as iron sulphide, and the ammonia fixed as ammonium sulphate, so that all odour is entirely dissipated.

The organised germs themselves are enveloped in the precipitate of ferric oxide, and are to a large extent carried down in the deposit and rendered innocuous—the importance of which fact will be admitted. Thus, in presence of certain substances, ferric sulphate behaves as an oxidising agent, the ferric oxide being reduced to ferrous oxide, which rapidly absorbs oxygen from the air. In view of these properties, ferric sulphate is suitable for a variety of uses.

B. DISINFECTING CESSPOOLS.—For this purpose ferric sulphate may advantageously replace the zinc chloride, copper sulphate, and ferrous sulphate generally used. It is employed, in a powdered condition, at the rate of 4 to 8 lbs. per cubic yard.

C. TREATMENT OF WASTE SEWAGE WATER.—This reagent is employed in several works for treating waste sewage water, the addition of ferric sulphate deodorising the liquid and giving an abundant precipitate, which, when treated in a filter-press, furnishes cakes rich in nitrogen.

D. DISINFECTING URINALS, BARRACKS, HOSPITALS, AND INSALUBRIOUS PREMISES.—Sprinkled about in powder, ferric sulphate is a very useful disinfectant for places where human or other egesta are deposited, such as urinals, cesspools in public conveniences, railway stations, schools, barracks, hospitals, prisons, etc. The usual dressing is at the rate of 3 to 6 ozs. per square yard of surface covered.

In time of epidemic this salt should be used in the state of a dilute solution for watering the streets and gutters of insalubrious districts.

For hospital use it should be employed not only in the cesspools, but also in the washing water, ventilation pipes, bed-pans, spittoons, etc.

In works where insalubrious trades are practised, and wherever unstable organic matters are treated—such as tallow melting, for example—ferric sulphate may be used to disinfect the raw materials employed. It is also very useful in cleansing establishments like breweries, distilleries, etc., where great care has to be devoted to the destruction of putrefactive germs. For stables, etc., a 1 per cent. solution is suitable for swilling the place down. For medical operating theatres and dissecting rooms, ferric sulphate is free from the dangers attending mercury dichloride.

For household use it may be advantageously placed in the drains removing waste waters, etc. liable to putrefaction, the briquette form being very useful for this purpose.

E. PRESERVING ANATOMICAL SPECIMENS.—As Messrs. Buisine have shown, ferric sulphate may be used for preserving anatomical specimens, and for enabling putrescent specimens to be handled without danger. Similarly, the dead bodies of animals killed by infectious diseases should be covered with this salt at the time of burial.

F. DISINFECTING MUD, SWEEPINGS, ETC.—Ferric sulphate is just as good for this purpose as ferrous sulphate, which has already been mentioned in this connection.

G. COAGULATING BLOOD.—Normal ferric sulphate can be used for coagulating blood, but it is preferable to employ a concentrated solution strongly acidified with sulphuric acid. A very suitable solution is met with in commerce under the name of *coagulant*, which has already been mentioned in dealing with the preparation of *rouil* mordant.

The method of application is very simple, the coagulant being poured on to the blood in a vat and the whole intimately mixed by stirring. A pasty mass forms directly, and may be filtered in a press or spread out on the ground to drain. The resulting cakes contain about 12 per cent. of nitrogen and 1·5 per cent. of phosphoric acid, and are therefore of considerable commercial value. The quantity of coagulant used is 1 volume to 20 of blood.

H. MIXTURES OF FERRIC SULPHATE AND OTHER ANTISEPTICS.—We have seen that ferric sulphate prepared by the Buisine process sets like plaster when mixed with a small quantity of water, a property which may be utilised for making briquettes containing any other known antiseptics, such as salts of copper, zinc, mercury, or potassium permanganate, phenol, etc.

With phenol, for example, the manufacture is very simple, the phenol being emulsified in the water required for treating the ferric sulphate. The resulting paste is then cast into moulds, where it sets rapidly and forms hard briquettes, the constituents of which dissolve slowly when brought in contact with water. The association of ferric sulphate with phenol forms a powerful disinfectant capable of rendering great service, especially in hospitals. In fact, this is the best and most convenient method of utilising phenol for this purpose.

These examples could be multiplied, but are sufficient to illustrate the interest attaching to ferric sulphate as a disinfectant and antiseptic.

156. **Purifying Waste Liquors, Drainage Waters, etc.**—For this purpose ferric sulphate forms an excellent reagent, conclusive results having been obtained from the experiments on the water of the river Espierre—which receives the drainage of the towns of Roubaix and Tourcoing—carried out by the French Government Department of Roads and Bridges at the Grimontpont works. The degree of impurity of the liquid there treated will be evident from the subjoined analyses:—

Description of Constituents.	1	2	3	4	5	6
	grms.	grms.	grms.	grms.	grms.	grms.
Fat	2·00	1·98	1·94	0·12	1·82	1·60
Organic matter, insoluble in acids . .	0·88	0·77	0·84	0·05	0·79	0·69
Soluble organic matter, colouring the water straw-yellow	0·58	0·03	0·17	0·07	1·04	1·46
Sodium sulphate	0·41	0·32	0·31	0·02	0·14	0·42
Sodium chloride	0·29	0·25	0·22	0·01	0·11	0·31
Alkali carbonates (K_2CO_3, Na_2CO_3) .	0·60	0·28	0·47	0·02	0·15	0·62
Calcium carbonate	0·90	1·28	1·20	nil	2·04	1·08
Sand, alumina, iron oxide, etc. . .	1·19	1·09	1·15	0·06	1·31	0·97
Dry residue per litre . .	6·85	6·00	6·30	0·35*	7·40	7·15

* This sample was taken on a Sunday when the factories were not working.

N.B.—These analyses are taken from the report of the committee on purifying the water of the Espierre (1881).

The following table, cited by Buisine, shows the excellent results of treating the above water with ferric sulphate:—

Espierre Water, 21*st April* 1892.

Constituents.	Sample drawn at 8.30 a.m.			Sample drawn at 3 p.m.		
Content per litre.	Crude Water.	Water purified with 4 kilos. of Slaked Lime per cub. metre.	Water purified with 1 kilo. of Ferric Sulphate per cub. metre.	Crude Water.	Water purified with 1·5 kilos. of Slaked Lime per cub. metre.	Water purified with 0·4 kilo. of Ferric Sulphate per cub. metre.
	grms.	grms.	grms.	grms.	grms.	grms.
Dry residue . . .	5·75	3·70	2·10	3·20	1·65	1·06
Mineral residue . . .	1·95	2·90	1·80	1·60	0·99	0·91
Fat	2·08	...	...	0·72	...	...
Organic matter in solution (expressed as crystallised oxalic acid) . . .	1·35	1·20	0·22	1·10	0·86	0·12
Alkalinity (expressed as CaO)	...	0·80	neutral	...	0·26	neutral
Weight of dry precipitate obtained from the process	...	6·96	4·29	...	3·03	1·90

The average composition of the air-dry purification sediment furnished by the ferric sulphate from Espierre water at the Grimontpont works was—

Water	20·90
Mineral matter (sand, clay, ferric oxide)	30·63
Fat	30·00
Nitrogenous organic matter	18·47
Total	100·00

The fat is derived from the numerous wool-combing works in Roubaix and Tourcoing, or from the household waste thrown down the drains, and is therefore different from wool fat (*suint*). It may be extracted from the sediment by means of carbon disulphide, and purified by distillation with superheated steam, followed by fractionation into a series of products utilisable partly in stearine manufacture, partly for soap-making, and partly as lubricants.

The residue left after extraction contains—

Ferric oxide	25·35
Clay, sand, etc.	37·05
Nitrogenous organic matter (containing N = 2·92 per cent.)	37·60
	100·00

and thus forms a fairly nitrogenous *poudrette* highly useful as an agricultural fertiliser.

Ferric sulphate has been applied, with equal success, to a large number of waste waters from manufacturing processes, and may be particularly recommended for purifying those of *starch factories*, *distilleries*, *sugar works*, *breweries*, *yeast factories*, *glue works*, *gelatine works*, *paper works*, *dye works*, *tanneries*, *wool-washing factories*, *slaughter-houses*, etc., etc.

The *modus operandi* is very simple, and consists in stirring into the water to be treated sufficient ferric sulphate solution to ensure the complete and rapid deposition of the resulting precipitate. After settling, the clear liquors are run off, and the residue is removed for use as manure on account of its nitrogen.

The ferric sulphate is dissolved in 5 or 6 times its own weight of water in a wooden vat, and heated by steam blown in through a leaden pipe. When as much as possible has been dissolved, more water is added to bring the solution down to 10 per cent. strength.

For the preliminary tests the solution may be prepared from 100 grms. of the salt in a 1-litre flask.

The next point is to determine how much of the solution should be added to the water under treatment.

For this purpose three 1-litre samples are taken, one being treated with 5 c.c. of the ferric sulphate solution, the second with 10 c.c., and the third with 15 c.c. All are then stirred, and note is taken which precipitates the best, the result showing whether ½, 1, or 1½ kilos. of ferric sulphate is required per cubic metre of the water.

Usually, the fact of the filtrate draining easily and free from smell indicates that sufficient ferric sulphate has been employed. The quantity and method of application depend on the position of the works, and on the nature and volume of water to be purified, but the following figures will serve as a general guide:—

Waste water from starch works . .	2–10 lbs. per cub. yard,
Red water from starch works . .	2–6 ,, ,,
Water from distilleries . . .	4–8 ,, ,,
,, wool-washing . . .	4–6 ,, ,,
,, breweries	4–6 ,, ,,

In the case of waters with an *acid* reaction, such as those from distilleries, dye works, etc., they must be neutralised with lime before the ferric sulphate is added. On the other hand, *alkaline* or *neutral* water (from starch works, wool-washing, sugar works, breweries, paper works, glue works, etc.) can be treated with the ferric sulphate at once.

If the works be situated in a town and have no open space available in the vicinity, the waste waters may be run into a masonry reservoir, where they are agitated by suitable means and, after the addition of the necessary amount of ferric sulphate, are immediately passed through a filter-press.

Wool-washing liquor may furnish, per 22,000 gallons (100 cubic metres), about 450 to 650 lbs. of dry residues, which, on issuing from the filter-press, contain 60 to 65 per cent. of moisture, and occupy a volume of 25 to 35 cubic feet.

Some of the precipitates are very difficult to filter in the press, and in such case only very thin cakes can be made. Before going to the expense of setting up a filter-press, experiments should be made to see whether this artificial aid is of any use. When the works has vacant land near by, settling basins may be made by digging out shallow pits of about 1000 square feet area and 16 to 20 inches deep, the excavated earth being banked up about 40 inches high all round so as to form basins 60 inches in depth. In addition to this there should be a masonry tank, large enough to collect one day's waste, at the works, from which tank the liquid can be raised in 2 to 3 hours and delivered through a cast-iron main, or, better still, suspended wooden troughs, to the settling basins. The latter can then be at some distance from the works.

A small pipe from the ferric sulphate tank can be led into the suction pipe of the pump and the outflow regulated by a tap so that the solution tank and the collecting tank will be discharged together. In this way the pump acts as a mixer, and the water is discharged into the settling basins, where the precipitate will come down in a single night, so that the clarified water is run off every morning and the basin filled with a fresh supply.

After about 20 operations the sediment will have attained a depth of 16 to 20 inches, the liquid is run into another basin, and the sediment drained by means of gutters. When the mud has thickened to a certain extent it is gradually shovelled out and spread on and round the banks, where it dries and can then be removed for use as manure.

In summer-time a couple of these basins, large enough to hold a day's output in addition to the sediment, will be enough; but in winter, when drying is more difficult, a larger number will be required.

In view of the necessity of shovelling the sediment on to the banks to dry, it will save labour if the basins are made long and narrow.

The liquid may also be pumped into a series of basins in communication with one another, in which event, if the traverse is sufficiently long, the liquid will run out clear from the end basin. In this case only a small centrifugal or other continuous pump will be required.

The cost of purifying with ferric sulphate is very low, this product being obtainable at 2s. to 3s. per cwt.

§ 3. APPLICATIONS OF MIXTURES OF IRON AND ALUMINIUM SULPHATES

157. **Manufacture of Fuming or Nordhausen Sulphuric Acid.**—*A.* INTRODUCTION.—Sulphuric acid was first prepared by calcining ferrous sulphate or green vitriol, hence its name *oil of vitriol*; and this process is still carried on for certain special purposes. The acid so obtained is in a highly concentrated state, and represents a solution of sulphur trioxide in 66 Bé. sulphuric acid; it is used in the manufacture of certain varnishes, for dissolving indigo, and in the alizarine colour industry.

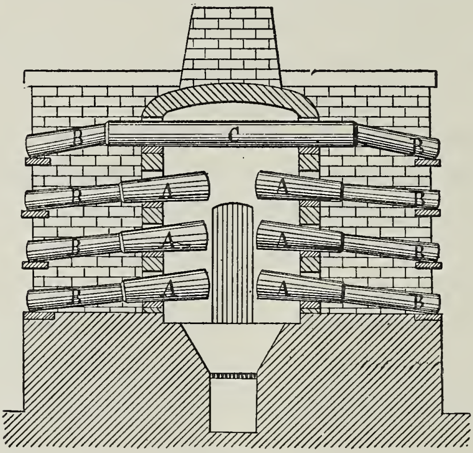


FIG. 193.—Gallery furnaces for the manufacture of Nordhausen sulphuric acid.

Formerly the manufacture of this acid was concentrated at Nordhausen in the Harz District, whence its name; but afterwards large works were established in Bohemia by J. D. Starck.

The production of this substance is intimately connected with that of the green vitriol extracted from pyritic shale.

B. MANUFACTURE.—(1) *Preparation of Vitriol Stone.*—The crude material is furnished by Prziban shales belonging to the

Silurian formation, which are scattered about in small aggregations in the pits of clay shale. Only such as are bituminous and contain from 1 to 20 per cent. of pyrites are used.

The mineral is first concentrated by levigation. Formerly it was preferred to calcine the pyritic shale in contact with air in earthenware retorts. In this manner from 12 to 14 per cent. of sulphur, suitable for different purposes, was obtained, and the residue was already partly decomposed. Later, however, it was desired to utilise the whole of the sulphur for the special object in view, and for this purpose the mineral was spread on an impervious flooring and exposed to the action of air and moisture for several years, thus oxidising the pyrites and producing sulphates of iron and aluminium (see Chapter IV., § 2).

When sufficiently oxidised the heaps are sprinkled with water, and the liquor is drained into large tanks where it clarifies. It has a density of 18° to 23° Bé., and consists principally of ferrous sulphate, ferric sulphate, and aluminium sulphate.

The next stage is to concentrate the liquor to 40° Bé. in order to extract the ferrous sulphate by crystallisation. The mother liquor is re-evaporated in iron pans to a syrupy consistence, and is then poured out on to a made floor.

The concentration is carried so far that the mass sets hard on cooling, and furnishes a hard greenish-yellow product (vitriol stone), which consists mainly of ferric sulphate, ferrous sulphate, and aluminium sulphate.

From 15 to 20 parts of pyritic shale are needed to furnish 1 part of vitriol stone. This residue is placed in roasting furnaces, where it is heated at a low temperature, and is stirred up in order to complete the oxidation of the ferrous sulphate, after which it is distilled.

The constituent sulphates present are by no means of equal value for the manufacture of fuming acid. The ferric sulphate is the best in this respect, and, in fact, is the only one which will part with the whole of its sulphuric acid without the latter undergoing decomposition—

$$Fe_2(SO_4)_3 = 3SO_3 + Fe_2O_3.$$

The ferrous sulphate, on the other hand, is first converted into ferric sulphate, half of its sulphur being given off as sulphur dioxide, which in this case is wasted.

Finally, aluminium sulphate will not part with its sulphuric acid except at a temperature whereat this latter is decomposed into oxygen and sulphur dioxide. Consequently the best vitriol stone for distilling is one containing the largest possible amount of iron in the state of ferric sulphate.

(2) *Distillation.*—The decomposition of ferric sulphate necessitating a high temperature, the stills have to be made of crucible clay, and small enough in size for the heat to penetrate all through. They are slightly conical in shape (A, Fig. 193), about 8 inches in diameter and 30 inches long, and are arranged in three or four rows around the gallery furnace, each of them corresponding to a condenser B of practically equal size. Each still is embedded in the wall of the furnace, and the condensers are supported by iron plates. The neck of each condenser engages in that of the corresponding still, and the joint is luted.

Usually the furnace contains 272 small stills, in addition to which a row of large stills, C,—extending right across the furnace, and each containing 32 small stills,—is sometimes arranged in the upper part of the furnace, in which event there are altogether 304 stills. The furnace is heated by 1 or 3 fires.

Each still is charged with 3 kilos. (6·6 lbs.) of broken vitriol stone. When they are all charged, gentle heat is applied by burning dried pinewood. At the end of about 4 hours distillation commences, water vapour, with traces of sulphur trioxide and sulphur dioxide, coming over first. As soon as the white vapours of sulphur dioxide appear, the condensers, which contain a little water, or 66° Bé. acid, are connected up, and the temperature is gradually raised to white heat. The operation takes 24 to 36 hours.

When the distillation is finished the reservoirs are taken away without being emptied, and the stills are emptied in order to be refilled and the operation repeated, which furnishes a fresh quantity of trioxide to enrich the acid already collected. When this acid is sufficiently charged with trioxide to measure 79° or 80° Bé., it is placed in stoneware vessels and left for about a week to clarify.

The condensers are then re-charged with 500 grms. of water, or 190 c.c. of 60° Bé. acid. In the former case four or five distillations are required to produce 79° Bé. acid; in the latter event, three or four distillations will give 80° Bé. acid. The acid is stored in stoneware vessels, closed by a stoneware stopper luted with wax.

For every 100 parts by weight of acid there remain about 125 parts of nearly pure iron oxide, known as *Caput mortuum*, *Colcothar*, etc., which is employed for polishing glass, as a pigment, etc. For the latter purposes it is calcined in closed vessels with or without an admixture of common salt, and is supplied in 57 different shades, ranging from blood-red to Havana brown (Sorel, article on "Chemical Products" in Fremy's *Encyclopédie*).

(3) *Cost Price.*—To obtain 1 cwt. of fuming acid, about 2½ cwts. of vitriol stone and 1 ton of fuel (lignite) are required.

According to Payen, the cost of manufacture is as follows:—

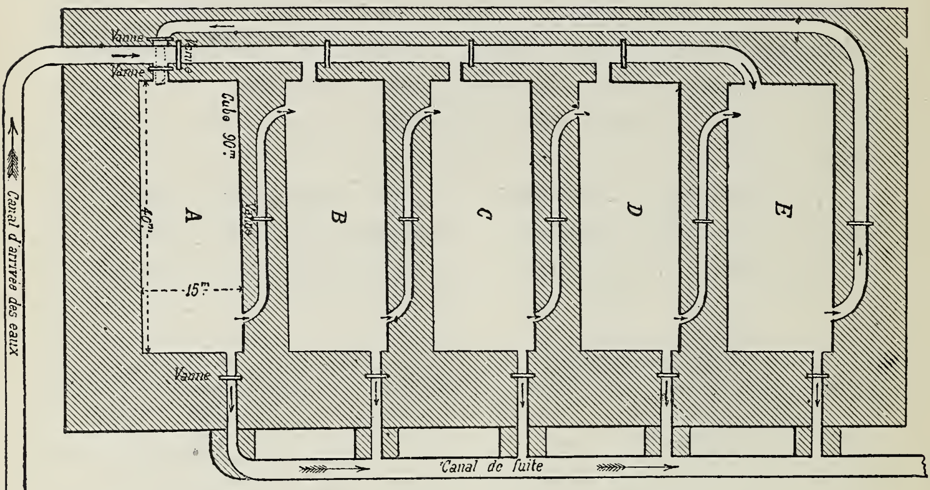
	s.	d.
Dried iron sulphate, 2½ cwts.	5	6
Fuel (lignite), 1 ton	1	3
Labour	3	2
Repair to plant	0	10
Interest	0	9
Total	11	6
Less value of residue	0	10
(Sorel.) Nett cost of 1 cwt. fuming acid	10	8

158. **Purifying Waste Water from Manufactories with Mixtures of Aluminium Sulphate and Iron Sulphates.**—These mixtures, generally waste products, have been successfully applied to water purification. The residual liquors from the manufacture of alum and ferrous sulphate from lignites have been, and still are, used in sugar works, distilleries, starch works, tanneries, etc. Their composition has already been described (Part II., Treatment of Lignites).

M. Vivien, of St. Quentin, has taken great interest in the utilisation of these residual liquors, and the following notes are extracted from his work on the purification of waste waters from factories and sewage waters.

The waste waters from starch works, distilleries, sugar works, etc. are contaminated with mineral matters (earth and inorganic salts) and various organic substances, soluble and insoluble.

The changes produced in the watercourses into which these waste waters are discharged are principally due to the organic substances in question. Such as are soluble act immediately, whilst the insoluble substances undergo decomposition, which in turn converts them into the soluble and more injurious condition.



Vue en plan d'une série de bassins isolés et indépendants.

Fig. 194.—Purification of waste waters. Plan of a series of isolated and independent decantation basins.

Vanne = sluice ; *Canal d'arrivée, etc.* = feed conduit ; *Canal de fuite* = outflow channel.

The germs of inferior organisms, such as *bacteria*, *monads*, *mucors*, *mucedinae*, all abundantly disseminated in nature, act in contact with air ; others, such as *vibrios*, *spirilla*, *bacilli*, etc., act in the absence of air, the result in both cases being the decomposition of the organic matters, even cellulose, with the formation of micro-organisms and more or less fœtid gaseous products.

If the decomposed matter is non-nitrogenous a liberation of carbon dioxide and hydrocarbons occurs, and water is produced along with acetic acid, oleaginous and humous products of various kinds. In the case of organic matter containing nitrogen and sulphur, a liberation of sulphuretted and phosphuretted hydrogen and production of ammonia and nitric acid will be noticeable.

Concurrently, the watercourse will become infested with special kinds of algæ, *hypheothrix* being the first to appear, and followed by *beggiatoa*, *leptomitus*, *spirogyra*, and finally by *cladophora*, the forerunner of purification. Aquatic plants disappear at the outset, but again come upon the scene when the water is once more in a pure state.

To obviate the foregoing inconveniences, the water must be purified and afterwards aërated, either by allowing it to flow thinly over the surface of a meadow or by filtration through a porous soil. To obtain the destruction of organic matter, however, this filtration must be gradual, and a soil that is too permeable is therefore unsuitable.

Waste water from manufactories ought to be purified immediately it leaves the works, and before any internal change begins. This is very important.

In order to obtain thorough purification of the water from beet-sugar refineries, the following conditions—which are subject to modification to meet the requirements of each particular case—should be fulfilled:—

(1) The water from the pulp presses should be purified separately before use in washing the beet; and in default of a thoroughly efficient method of purification for that purpose, or to fit the water for discharge into a watercourse, it should be treated by known means, and turned on to the land or oxidised by running it for a sufficient distance over the meadows. The press water represents about 6 to 9 gallons per cwt. of beet, or 1400 gallons per 100 tons; and enough ground is generally available to oxidise this quantity after the necessary clarification.

(2) The other waste waters should be united and treated with lime, either alone or with a salt of iron or alumina, followed by lime to render them alkaline. The residual liquors from the manufacture of alum and ferrous sulphate from lignites may be successfully employed for this purpose, in the proportion of 1

part of 32° Bé. liquor per 1000 parts of beet; after the water has travelled a distance of about 10 yards the metallic salts will have had time to act, whereupon sufficient 10° to 15° Bé. milk of lime is added to completely decompose the iron and alumina salts, and to impart a slightly alkaline character to the liquor, which then deposits a flocculent sediment and clarifies. The degree of alkalinity (expressed in terms of CaO) should vary between 100 and 200 m. grms. per litre.

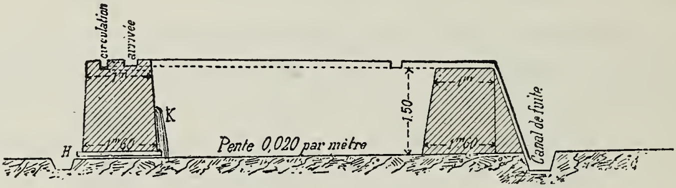


Fig. 195.—Vertical section of decantation basin.

Arrivée=supply; *Pente*=gradient; *Canal de fuite*=outflow.

Treated in this manner, the waste waters from sugar works are rendered easy of decantation. The operation is performed in a series of basins, each of which can be isolated from the system when full, the waters being delivered through a channel with a fall of about 20 per 1000. The arrangement of these basins is shown in Figs. 194, 195. Here A, B, C, D are the basins, varying in number and size according to the quantity of matter to be precipitated, the dimensions being chosen so that each basin can be filled in the shortest possible time—10 to 15 days—according to the susceptibility of the sediment to decomposition. The waters settle in the first basin, and then pass in turn through the second, third, and others in the series, being only discharged into the outflow when perfectly limpid—for instance, after leaving the basin C. At this stage they should be slightly alkaline to test paper. If they can then be made to overflow the surface of a plot of ground in a thin layer, *e.g.*, used for irrigating meadow land or filtered through permeable soil, they will be inoffensive, well aërated, and purified to the fullest extent.

When the first basin of the series is full the supply is stopped and the impure waters are delivered into the second basin (B), and so on to the end of the series, the end basins being placed in communication, by means of a conduit, to establish a continuous circulation and recommence a fresh series when the last basin has been reached.

Where the available ground space is large enough for a sufficient number of basins to hold the whole of the deposits there is nothing further to do; but if space is limited, each basin will have to be emptied when shut off from the rest, and cleaned out for use over again.

If the basins are above ground—which is preferable to sinking them below the surface—they are easy to drain and empty, it being sufficient to lay a few (8-inch) earthenware pipes, H, on the lower side of each basin, and cover the inner ends with faggots to serve as a filter and prevent obstruction. While the basin is in use these pipes are closed with plugs, which are removed when the work of discharging the deposited mud is commenced. The sloping bottom allows the water to drain away, and a breach can be made in one of the banks in order to clear out the mud.

In sugar works the acidified waters from the triple-washing process should be completely neutralised before they are run into the collecting tank, lime or even chalk being suitable for this purpose.

In factories where caustic soda is used for washing the utensils, the waste liquids should be stored separately, and not run off until they have been neutralised by some acid.

The cost of purifying the waste waters of sugar works, for example, by means of alum waste liquor, may be put down as follows per ton of beet treated in the works:—

Reagent, 2·2 lbs. at 32s. per ton . .	= 0·4d.
Lime, 22 lbs.	= 0·14
Labour	= 0·18
Total . . .	0·72d.

or, taking 500 gallons as the volume of waste water from treating 1 ton of beet, the cost will be 0·14d. per 100 gallons treated.

The pasty mixture or magma obtained by evaporating the extract from oxidised lignites, and consisting of a very impure aluminium sulphate with a large proportion of ferric and ferrous sulphate (see Part II., Chap. III.), may also be used for this purification.

Trials have been made with this sulphate in the vicinity of the large collecting basin at Clichy, about 2 lbs. being used per 1000 gallons of sewage water. That the results are fairly satisfactory will be evident from the following table, the figures being averages for a working period of nine months:—

Constituents.	Total Weight per cub. metre (220 galls.) of Sewage Water.	Weight left after Purification.	Weight of Substance removed by Purification.
	kilos.	kilos.	kilos.
Nitrogen	0·033	0·014	0·017
Phosphoric acid	0·013	...	0·013
Potash	0·028	0·028	...
Soda	0·116	0·116	...
Organic matters	0·657	0·101	0·574
Mineral ,,	1·898	0·595	1·421
Total	2·745	0·854	2·025

The oxidised lignites themselves have also been used for the same purpose, by the Houzeau and Devedeix method, which consists in thinning down the lignite with water and pouring it into the waste water under treatment, a certain quantity of milk of lime being then stirred in. A coagulum forms, and the substances are rapidly precipitated. The quantity of lignite required varies from 1 to 3 grms. per litre (1000 grms.) of waste water treated.

159. **Utilising Pyritic Lignites for Fertilising and Improving Soils.**—The oxidised pyritic lignites, and even the lixiviation residues from the same, are still largely employed in agriculture, though nothing like to the same extent as they were thirty years ago.

The virgin cinder or unextracted oxidised lignite is applied at the rate of about 12 bushels per acre, chiefly for meadow land or artificial grasses. It acts by virtue of its ferrous sulphate, and produces the same result as this latter. On artificial grasses it has the same effect as gypsum, and is very useful. Moreover, containing 0·3 to 0·5 of nitrogen, though in a slowly assimilable form, it also possesses a certain value as a nitrogenous manure.

The lixiviated cinder is applied to the same uses, but the dressings are much larger, namely 60 bushels per acre.

Both kinds of cinder are largely used in the vine districts of Champagne, where they are made into compost with stall manure, sweepings, mud, etc. When mixed with fossil phosphates they render a portion of the phosphate soluble and assimilable, and fairly good results have been obtained by treating stall manure with this mixture.

Pyritic lignite or cinder should be used on calcareous sandy soils, the dressing being applied in autumn or spring.

PART IV

CHEMICAL CHARACTERISTICS OF IRON AND ALUMINIUM. ANALYSIS OF VARIOUS ALUMINOUS OR FERRUGINOUS PRODUCTS.

CHAPTER VII

ALUMINIUM

§ 1. CHEMICAL CHARACTERISTICS OF THE ALUMINIUM COMPOUNDS

160. **General Reactions of the Aluminium Salts.**—Solutions of aluminium salts are generally acid to test paper.

Caustic Alkalis give with aluminium salts a white gelatinous precipitate soluble in excess of the reagent.

Ammonia completely precipitates alumina in the state of hydroxide, when the precipitation is effected in presence of ammonium chloride and boiled until all the excess of ammonia has been driven off.

The Alkali Carbonates give a white precipitate of alumina, with liberation of carbon dioxide, and the precipitate is insoluble in an excess of the reagent.

Oxalic Acid and *Alkali Oxalates* do not precipitate aluminium salts.

Sodium Phosphate throws down a white precipitate of hydrated aluminium phosphate, which is difficult to identify owing to its great resemblance to alumina, being gelatinous and soluble in both caustic alkalis and acids.

Barium Carbonate and *Calcium Carbonate* in considerable excess precipitate alumina, even in the cold; the reaction is slow at the ordinary temperature, but rapid at boiling heat.

Sulphuretted Hydrogen gives no precipitate with aluminium salts, but ammonium sulphide completely precipitates aluminium in the condition of hydroxide, with liberation of H_2S.

Sodium Hyposulphite (thiosulphate) completely precipitates alumina in the warm, and when the reagent is in excess.

A somewhat characteristic reaction is obtained by evaporating aluminium sulphate in presence of an excess of potassium sulphate; alum is formed, crystallising in cubes or octahedra.

Aluminium can be readily detected by microchemical means. One exceedingly delicate reaction is to precipitate the aluminium salt as a *cesium alum* (Cs_2SO_4, $Al_2(SO_4)_3$, $24H_2O$), the limit of sensitiveness being 0·3 micromilligram of aluminium.

Aluminium is easily distinguished before the blowpipe, by furnishing a fine blue coloration when heated along with cobalt nitrate. This reaction is characteristic, provided the mass does not fuse, a blue fusible bead not being distinctive of this metal.

161. **Estimation of Aluminium.**—The metal is estimated in the condition of *alumina*. When combined with nitric or hydrochloric acid it is thrown down, as hydroxide, by adding ammonium chloride, boiling, and, after removal from the flame, treating with ammonia, which gives a gelatinous precipitate impregnated with ammoniacal salts. After re-boiling to expel the excess of ammonia, the liquid is left for the precipitate to subside, and is then filtered. The precipitate is washed by decantation, until the washings cease to leave a residue when a portion is evaporated on a strip of platinum. After drying at 100° the filter and precipitate are calcined in a covered platinum crucible, the cover being removed when it is certain that all moisture has been expelled.

Ammonium Sulphide is a good precipitant for this metal, but not in presence of other metals precipitable by the same reagent. Moreover, there is always the risk of a portion of the sulphide oxidising during filtration, and forming an insoluble aluminium sub-sulphate which is difficult to decompose by calcination, in which event the weight of alumina is somewhat in excess of the truth.

If the precipitation by ammonia be effected in presence of *sulphuric acid*, the formation of insoluble sub-sulphates will occur, and the final traces of sulphuric acid will be difficult to eliminate in calcination. When this accident is feared, the precipitate must be re-dissolved in hydrochloric acid and thrown down anew with ammonia.

Sodium Hyposulphite (thiosulphate) is a good precipitant for alumina in presence of sulphuric acid.

The volumetric estimation of alumina has also been proposed.

Aluminium phosphate is insoluble in acetic acid in presence of alkali phosphates; and a weak solution of alumina, too dilute for detection by ammonia, will still give a decided turbidity on the addition of a phosphate. Aluminium phosphate only exhibits the constant composition $Al_2(PO_4)_2$ when the aluminic solution is treated with sodium acetate and poured into a solution of a tribasic phosphate acidified with acetic acid, otherwise the precipitate will be of variable composition.

On this reaction Fleischer founded the following volumetric method of estimating alumina:—

The aluminic solution is treated with sodium acetate and poured into a burette—having previously, if alkaline, been saturated with HCl—and is then run, drop by drop, into a standardised phosphate solution. To ascertain whether the end point of the reaction has been attained, it is necessary to filter a few drops of the phosphatic liquid at intervals and see whether it still gives a turbidity with the aluminium solution. An alcoholic solution of *brasiline*, which gives a violet-blue coloration with a slight excess of aluminium acetate in the warm, may also be used as indicator.

The phosphate solution is prepared by dissolving equal parts of ordinary (uneffloresced) sodium phosphate and sodium acetate to form a decinormal solution (Fleischer).

162. **Separating Aluminium from other Metals.** — Aluminium may be separated from the *alkali metals*, *calcium*, and

magnesium by precipitation, as alumina, with ammonia in presence of ammoniacal salts. The *alkali salts*, the *calcium*, and the *magnesium* remain in solution; but if a large proportion of *calcium* be present a portion may be carried down along with the alumina, or precipitated by the carbon dioxide in the air.

When *barium* and *strontium* are present they must be removed by sulphuric acid before proceeding to the precipitation of the alumina.

If the *aluminium* and *calcium* are in the form of nitrates they may be separated by evaporation and heating to 170°–180° C., whereupon the aluminium nitrate decomposes, with liberation of nitrous fumes, whilst calcium- and magnesium nitrate remain almost unchanged. On taking up the mass with concentrated ammonium nitrate, the whole of the calcium and magnesium will re-dissolve, leaving the aluminium hydroxide entirely insoluble.

For separating aluminium from phosphoric and arsenic acids, the first-named must be in the state of nitrate or chloride. The liquid is evaporated, along with an excess of H_2SO_4, until the appearance of white fumes. After cooling, a concentrated solution of aluminium is added, and the liquid shaken up, whereupon alum is formed, and is thrown down by alcohol. On filtering after several hours' rest, the arsenic and phosphoric acids pass away in the filtrate. Sometimes a small quantity of alumina escapes with the acid solution; this can be tested by neutralising the phosphoric acid with ammonia and precipitating with ammonium sulphide, the remainder of the alumina coming down as oxide.

Aluminium can be separated from zinc, nickel, or cobalt by adding sodium carbonate, followed by potassium cyanide and digestion in the cold. The carbonates dissolve and the alumina is collected on a filter, but must be re-dissolved in acid and re-precipitated before weighing, in order to free it from alkali. Sodium hyposulphite is employed to separate *aluminium* from *iron* and *manganese*, an excess of this reagent, in the warm, throwing down alumina completely, but retaining iron in solution as a double hyposulphite.

The aluminium and iron being dissolved in hydrochloric acid or sulphuric acid, the excess of free acid is nearly neutralised, and water is added to reduce the content of the two oxides to below 0·1 grm. per 50 c.c. To this solution (*cold*) a slight excess of hyposulphite is added, and after decoloration has taken place heat is applied, and the liquid kept on the boil so long as an odour of SO_2 continues noticeable. The granulated precipitate is washed quickly, dried, calcined, and weighed. The alumina is always white (Gerhardt and Chancel).

Among other methods proposed, the following may be mentioned :—

(1) Separation by using NaHO or KHO.

(2) Fusion of the two oxides with NaHO or KHO.

(3) Reducing the oxides by hydrogen, and dissolving the iron in dilute hydrochloric acid.

(4) Treatment of the solution with H_2S or $(NH_4)_2S$ after an addition of ammonium tartrate or citrate.

An original method for separating aluminium and iron is that proposed by F. A. Gooch and F. S. Havens, and based on the fact that hydrated aluminium chloride (Al_2Cl_6, $12H_2O$) is but very slightly soluble in hydrochloric acid, whereas Fe_2Cl_6 is extremely soluble therein.

The mixed chlorides are dissolved in a minimum of water, and poured into a mixture of equal parts of ether and concentrated HCl, aluminium chloride being less soluble in this than in HCl alone. The liquid being kept at 15° C., is saturated with gaseous HCl, this being repeated after an addition of several c.c. of ether. The Al_2Cl_6 comes down and is filtered over asbestos in a Gooch crucible, then washed with the ether-HCl mixture, re-dissolved in water, and thrown down by ammonia for estimation as Al_2O_3. One part of Al_2O_3, corresponding to 5 parts of Al_2Cl_6, dissolves in 125,000 parts of the ether-acid mixture.

Vignon proposed to separate iron from aluminium by treating the mixed oxides with *trimethylamine*. This forms soluble trimethylamine aluminate, which is separated from the insoluble ferric oxide by filtration.

Ilinski and Knorre proposed another organic reagent, *nitroso-β-naphthol*, for this purpose, ferrous and ferric salts being thrown down from an acetic acid solution, whilst alumina remains dissolved. The method, however, is inapplicable when phosphates are present.

Electrolysis can also be successfully employed for separating aluminium from iron. The operation is performed in presence of a large excess of ammonium oxalate, with a current of about 1¼ ampères, care being taken to prevent a rise in temperature. In this manner aluminium may be separated from iron, nickel, cobalt, and zinc.

When the electrolysis is prolonged the aluminium is thrown down as hydroxide—*never in the metallic state*,—and in such event must be re-dissolved by an addition of oxalic acid (Classen and Ludwig, *Berichte*, 18, 1795).

The metals of the third group are separated *en bloc* by treating the mixture with potash in presence of tartaric acid. Sodium sulphide is then added, the liquid poured off after settling, and the precipitate filtered, sodium sulphide water being used for washing. The solution will contain only aluminium and chromium, which may then be separated by heating with potassium nitrate and fusing the residue with 4 parts of K_2CO_3 and 2 parts of KNO_3. The fused mass is treated with HCl and $KClO_3$, evaporated, and taken up again with water. On adding ammonia, alumina is precipitated, the chromium being left in solution.

Aluminium can be easily separated from the metals precipitable by sulphuretted hydrogen from acid solutions.

§ 2. ANALYSING ALUMINIUM PRODUCTS

163. **Analysis of a Clay or Kaolin.**—*A*. TOTAL ANALYSIS.—The substances to be estimated are—(1) hygroscopic moisture; (2) water of combination; (3) organic matter; (4) alumina; (5) ferric oxide; (6) silica and insoluble matter; (7) lime; (8) magnesia; (9) potash; (10) soda.

I. *Hygroscopic moisture* is determined by drying a sample at 120° C. until constant.

II. *Water of Combination and Organic Matter.*—The dried sample from I. is calcined at bright red heat, which removes the water of combination, organic matter, and carbon dioxide. The latter is estimated by the usual methods, and the difference gives water of combination and organic matter together.

III. *Silica and Insoluble Matter.*—The calcination residue is pulverised with care, and 1 grm. is mixed with 4 or 5 grms. of pure dry sodium carbonate in a platinum crucible, which is then gradually heated to bright redness. Alkali silicates and aluminates are formed, whilst the lime, magnesia, and ferric oxide are separated. When the mass is fused the crucible is cooled suddenly by standing it on a cast-iron plate or by immersion in cold water, which generally enables the contents to separate from the walls of the vessel. The whole is then placed in a porcelain capsule and treated with 15 to 20 parts of dilute hydrochloric acid. As soon as solution is complete the crucible is withdrawn and washed, the washings being united to the solution, and the whole evaporated to dryness. It is then taken up with water acidified with HCl, filtered, washed, calcined, and weighed, the result being the silica.

IV. *Alumina and Iron.*—-The washings from the preceding test are made up to a known volume, and an aliquot portion is taken and treated with a little bromine water to peroxidise the iron. After expelling the excess of bromine by boiling, ammonia is added in slight excess, this being next removed by boiling up again, after which the liquid is filtered, the precipitate washed by decantation and on the filter, and dried, calcined, and weighed. This gives the *alumina* and *ferric oxide* together, and the iron can then be estimated in the ordinary way. It is, however, preferable to work with another aliquot part of the solution and to acidify same with H_2SO_4, evaporate until white fumes appear, take up with water, reduce by means of zinc, and estimate the iron (as ferric oxide) with potassium permanganate. Alumina is taken by difference in either case.

V. *Lime, Magnesia.*—The filtrate from the precipitation of iron and alumina is treated with ammonium oxalate to throw down the lime; and, after removing the calcium oxalate by filtration, sodium phosphate is added, with the usual precautions, to precipitate the magnesia.

VI. *Potash, Soda.*—From 2 to 4 grms. of the substance under examination are weighed out and calcined, the residue being dissociated by means of sulphuric and hydrofluoric acids. Hydrochloric acid is then added, and the liquid made up to a known volume, an aliquot part of which is next treated with barium hydroxide and filtered. After washing, the excess of barium in the filtrate is thrown down by ammonium carbonate, re-filtered, and evaporated to dryness. The residue is calcined, taken up with water, again treated with ammonium carbonate, and filtered a third time, whereafter it is evaporated to dryness, calcined, and weighed, thus giving the sum of the two chlorides. The potash is separated by platinum tetrachloride, and the soda is then readily calculated.

Or the following method may be pursued:—

1 to 2 grms. of the product are mixed with a sixfold volume of ammonium fluoride, and heated to redness in a platinum crucible. The silica is volatilised as silicon fluoride, leaving the fluorides of calcium, magnesium, and the alkali metals, as residue. On treating these with H_2SO_4 they are converted into sulphates, which should completely dissolve in water acidified with HCl, and are then transformed into chlorides by precipitating the sulphuric acid with barium chloride. The iron and alumina are separated with ammonia, and the lime with ammonium oxalate; the liquid is then evaporated, and the residue calcined to expel the ammonia salts, leaving magnesia and alkali metals as chlorides. These can finally be separated in the usual manner.

B. PARTIAL ANALYSIS.—Clay intended for producing aluminium sulphate or alum can be analysed in a far simpler manner, which, however, is quite sufficient to determine its value for manufacturing purposes. Moreover, the method has the advantage of being a reproduction of the manufacturing process on a small scale.

A small sample (about 50 grms.) of the clay is placed in a tared porcelain or platinum capsule and moderately calcined. When the clay has attained dull red heat the capsule is withdrawn and weighed after cooling, the difference giving the *loss of weight on calcination.*

The powdered residue is then treated with 100 grms. of

60° Bé. sulphuric acid, the whole being well mixed and heated gently until it solidifies, thus converting the alumina into sulphate; whereupon it is extracted with boiling water, filtered, and the united liquids concentrated to about 35° Bé. This solution is next boiled with a slight excess of potassium- or ammonium sulphate and left to crystallise. When the capsule is cold the liquor is poured off, the alum being washed with a cold saturated solution of alum, and afterwards dried and weighed. The weight of alumina is ascertained by calculation (Pouchet).

164. **Analysing Bauxite.**—The constituents to be estimated are—(1) water and organic matter; (2) insoluble matter; (3) titanic acid; (4) ferric oxide; and (5) alumina.

I. *Water and Organic Matter* are determined by calcining 0·3 grm. of the mineral, beginning at gentle heat and finally before the blowpipe until constant.

II. *Insoluble Matter.*—1·5 grms. of mineral, ground and dried at 100° C., are treated with 50 c.c. of 42 Bé. sulphuric acid, and evaporated until white fumes are evolved. The mass is taken up with 100 c.c. of water, boiled for 10 minutes, then filtered and washed with hot water. The united filtrates should measure 175 c.c.

The insoluble residue is calcined and weighed. It consists mainly of silica, with a little titanic acid, ferric oxide, and alumina. To estimate the SiO_2, the insoluble matter is taken up with HF and H_2SO_4, evaporated, calcined, and weighed, the loss in weight being silica.

The new residue is fused with 1 grm. of potassium bisulphate, the cooled mass being returned to the beaker containing the sulphuric liquor from the original attack on the substance. The slight residue left consists of silica, which must be added to that already obtained.

III. *Titanic Acid.*—The volume of the sulphuric solution is made up to 250 c.c., and after agitation 50 c.c. of this solution (= 0·3 grm. of bauxite) are diluted to 300 c.c. and treated with 2 c.c. of HCl, followed by a slight excess of ammonia; then boiled for 5 minutes, filtered, and washed with boiling water. The precipitate, weighed after calcination, contains alumina, ferric oxide, and titanic acid.

To estimate the last-named, 100 c.c. of the sulphuric solution (= 0·6 grm. of bauxite) are treated with ammonia until a permanent precipitate is formed, this being then re-dissolved in a few drops of H_2SO_4, and the solution diluted to 400 c.c. If the solution contain much iron it will be of a yellow colour, and in such event is reduced by a current of SO_2 and boiled for an hour, a little of a saturated solution of SO_2 being added at intervals. The titanic acid precipitate is filtered, and washed with boiling water. If yellow, iron is indicated, and the mass must be fused with 1 grm. of $KHSO_4$, taken up with water, and the iron titrated with permanganate after reduction with zinc.

IV. *Ferric Oxide.* — 50 c.c. of the sulphuric solution are treated with 10 c.c. of dilute H_2SO_4 and 1 grm. of granulated zinc. After the reduction is complete the solution is titrated with permanganate. When the mineral contains but very little iron, 0·5 grm. must be taken. This is evaporated in a platinum crucible with 3 c.c. of 25 per cent. H_2SO_4 and 5 c.c. of HF until white fumes are given off, the excess of sulphuric acid being then expelled by heat. When cool the residue is taken up with water and 10 c.c. of dilute H_2SO_4, the liquid being then reduced by zinc and titrated with permanganate.

V. *Alumina.*—This is determined by deducting the weights of ferric oxide and titanic acid from the first precipitate obtained in Test III. (J. Otis Handy, *Industries and Iron*, vol. xxi. Nos. 1239–1241).

165. **Analysis of Alunite.**—Constituents estimated—(1) water and loss on calcination; (2) silica and insoluble matter; (3) potash; (4) alumina; (5) ferric oxide.

I. *Water and Loss on Calcination* are found by calcining 1 grm. of substance at moderate heat, preferably over a Bunsen flame, so as not to decompose the sulphates.

II. *Silica and Insoluble Matter.*—Two grms. of pulverised substance are treated with dilute HCl in a porcelain capsule; then evaporated to dryness, taken up with HCl and boiling water, filtered, washed, and calcined. The solutions are united and made up to a known volume.

III. *Sulphuric Acid* is determined by precipitating an aliquot portion of the clear liquid with barium chloride, the usual precautions being taken.

IV. *Alumina and Ferric Oxide.*—Another portion of the liquid is treated with bromine water to peroxidise the iron, which is thrown down, along with the alumina, by ammonia after boiling. The precipitate is washed, calcined, and weighed.

The iron is determined by treating a known volume of the liquid with H_2SO_4, followed by evaporation, reduction by zinc, and titration with permanganate. The alumina is then easily calculated.

V. *Potash.*—One grm. of substance is acted upon with HCl, the residue is removed and the liquid precipitated by barium hydroxide, the excess of which is afterwards removed by ammonium carbonate. After filtration, washing, and evaporation to dryness, the residue is taken up with water acidified with HCl, filtered again, evaporated, and the potash estimated by means of platinum chloride.

166.—**Analysis of Alumina.**—*A*. ALUMINIUM HYDROXIDE.—The following are determined—(1) water; (2) silica; (3) alumina; (4) soda.

I. *Water.*—One grm. of substance is calcined in a well closed crucible, the heat being applied gently at first, but afterwards by the gas blowpipe for 20 minutes. The loss in weight represents water and CO_2. This latter is afterwards calculated from the weight of soda found at a later stage, and is then deducted, the difference being water.

II. *Silica.*—Aluminium hydroxide is soluble in 42° Bé. sulphuric acid—prepared from 900 c.c. of concentrated H_2SO_4 and 1290 c.c. of water—which leaves silica unchanged.

Five grms. of substance are dissolved by heating with 25 c.c. of 42 Bé. acid, the liquid being then made up to 100 c.c. and boiled. After filtration the residue is washed, dried, and fused with 1 grm. of potassium bisulphate, after which it is cooled, taken up with water, filtered, washed, calcined, and weighed in a platinum crucible. This calcined residue is treated with HF and H_2SO_4, evaporated to dryness, calcined anew, and weighed; the difference between the two weights represents *silica* (J. O. Handy).

III. *Soda.*—One grm. of substance is treated with a mixture of nitric and hydrochloric acids. After boiling to drive off HCl the solution is evaporated to dryness, in a large platinum capsule, over a Bunsen burner until nitric vapours cease to come off. The residue is crushed and mixed with 1 grm. of pure NH_4Cl and 8 grms. of $CaCO_3$. It is then heated in a covered platinum crucible, the Bunsen flame merely touching the bottom during the first $\frac{1}{4}$ hour, after which it is raised to a bright red heat for 45 minutes. After cooling, the mass is treated with just enough water to make it friable, then powdered in a mortar and extracted with hot water, filtered, and washed, the filtrate being shaken up with a slight excess of ammonium carbonate. The calcium carbonate precipitate is filtered, the filtrate evaporated in a platinum capsule over the water bath, then heated to drive off the ammonia salts, re-dissolved in a little water, again treated with ammonium carbonate, shaken up, filtered, washed, evaporated, dried, gently calcined, and weighed. The result is sodium chloride, from which the weight of carbonate is ascertained by calculation (J. Otis Handy).

IV. *Alumina* is estimated by difference.

B. CALCINED ALUMINA.—Water and soda are determined as in hydrated alumina, the soda being calculated as Na_2O.

The silica is estimated by fusing 1 grm. of substance with 10 grms. of $KHSO_4$, the mass being taken up with water and filtered. The insoluble residue is calcined and then fused with 1 grm. of Na_2CO_3, the melt being taken up with 15 c.c. of water and 25 c.c. of 25 per cent. H_2SO_4 in a covered porcelain capsule, solution being followed by evaporation until white fumes appear. After cooling, the mass is treated with water, filtered, washed, dried, calcined, and weighed. The residue taken up by HF and H_2SO_4 is re-weighed after calcination, the difference giving the weight of silica.

167. **Analysis of Sodium Aluminate.**—In this case alumina and soda have to be determined. Gravimetric methods may be employed, but G. Lunge (*Monit. Scient.*, 1891, p. 285) recommends the following titrimetric method:—

A given weight of the aluminate is dissolved and diluted to a known volume, the insoluble residue being determined. One portion of the clear liquid is treated with phenolphthalein and titrated in the warm with normal HCl solution until decoloration occurs. This gives the amount of *soda* combined with alumina and silica. A drop of methyl orange is then added to the same portion of liquid, and titration is continued at 30° to 37° C. until the red tinge becomes permanently yellow, this change marking the end point of the *alumina* determination. The method gives highly satisfactory results, 26·08 per cent. of Al_2O_3 being found in one case instead of 25·92 per cent. furnished by the gravimetric method. With a pure product the latter method gave 2·818 grms. of Al_2O_3 per litre, and the volumetric method 2·8203 grms. A somewhat similar method was proposed by Bayer (*Zeits. Anal. Chem.*, 24, p. 542).

168. **Analysis of Aluminium Sulphate.**—The substances to be estimated are—(1) water; (2) insoluble residue; (3) alumina; (4) total sulphuric acid; (5) potash and soda; (6) iron; (7) free sulphuric acid.

I. *Water.*—This is easily determined by calcining the substance with great care.

II. *Insoluble Residue.*—2 to 5 grms. of substance are dissolved in distilled water, the insoluble portion being dried and weighed.

III. *Alumina.*—This is easily estimated from an aliquot part of the foregoing solution by means of sodium hyposulphite, the precautions already given being observed.

IV. *Total Sulphuric Acid.*—This estimation is performed on another aliquot part of the solution from II.

V. *Potash and Soda* are also determined from an aliquot part of the solution after eliminating the other constituents by the usual means.

VI. *Iron.*—When the substance is impure and contains much iron, that metal can be estimated by the permanganate method This is, however, rarely the case, the amount of iron being usually not more than traces, to which the titrimetric method is inapplicable. In such event colorimetry must be resorted to, and for this purpose it was at first proposed to employ potassium sulphocyanide and compare the colorations obtained.

According, however, to G. Krüss and H. Moraht, the resulting red coloration is not necessarily proportionate to the percentage of iron, but is greatest when the iron and the sulphocyanide are in equivalent proportions. The coloration is, in fact, due to a ferri-potassium sulphocyanide which is decomposed by water; and, its intensity being a function of the dilution, cannot serve as a guide to the percentage of iron present.

The equation

$$Fe_2Cl_6 + 6KCNS = Fe_2(CNS)_6 + 6KCl$$

does not exactly express the reaction corresponding to the maximum of coloration. In fact, 24 molecules of KCNS are required to 1 of Fe_2Cl_6, which indicates a double salt as the cause of the coloration, namely $Fe_2(CNS)_6$, 18KCNS, a salt crystallising, with $8H_2O$, to form hygroscopic prisms. On dilution it is decomposed into 12KCNS and another double salt, $Fe_2(CNS)_6$, 6KCNS, which crystallises in hexagonal prisms furnishing a lighter coloured solution of a more orange tinge.

Magnanini arrived at results slightly differing from these, but likewise indicating the unreliability of the process.

On the other hand, it has been experimentally proved by J. Riban that solutions of ferric sulphocyanide and coloured solutions of acetates and double tartrates of the alkalis are subject to progressive dissociation of the pigmentary salt, and, being therefore impossible of comparison with standards, are inapplicable to the colorimetric estimation (even approximately) of iron.

R. Tatlock's method of colorimetric determination with sulphocyanide is performed as follows:—The red solution is agitated in a tube with ether, and the resulting coloration is compared with those furnished by standard ferric solutions under the same conditions.

G. Lunge (*Monit. Scient.*, 1897, p. 160) gives the following method for estimating small quantities (only) of iron in aluminium sulphate by colorimetry:—

Use is made of tubes of very clear glass, with emery stoppers, and graduated, in $\frac{1}{10}$ c.c., to 25 c.c., their size (internal diameter, 13 mm.) being such as to leave plenty of room for shaking up the contents. Three at least are required for each test, but it is better to have five or six.

The reagents consist of—

(1) A $\frac{1}{10}$ solution of potassium sulphocyanide.

(2) Pure ether.

(3) A solution of ammonium ferrosulphate prepared by dissolving 7 grms. in 1 litre of water containing a little H_2SO_4. For use, 1 c.c. is diluted to 100 c.c., the new solution therefore containing 0·01 grm. per litre.

(4) Nitric acid, as free from iron as possible.

When the substance under examination is pure, 1 to 2 grms. are dissolved in a little water and treated with 1 c.c. of HNO_3, the liquid being made up to 50 c.c. after heating and re-cooling. At the same time, 1 c.c. of the nitric acid is also diluted to 50 c.c.

Five c.c. of the solution of substance are then placed in a test-tube, and an equal quantity of the dilute nitric acid in three or four other tubes, a variable quantity of the ammonium ferrosulphate being added to each, so as to form a scale of percentages which shall include that of the substance under examination.

Each tube receives a uniform addition of water and 5 c.c. of potassium sulphocyanide, whereupon coloration ensues; but as this is generally a dirty reddish yellow, and not in relation to the percentage of iron, each sample is treated with 10 c.c. of ether, and well shaken up. The compound sulphocyanide of potassium, iron, and aluminium is decomposed by the ether, which dissolves out the iron sulphocyanide alone, and is tinged in proportion to the amount of iron present. The aqueous solution should be completely decolorised; and as the colour of the ethereal layer progressively deepens, it is advisable to leave at rest for some hours before comparison, though not too long, as otherwise decoloration may set in.

The degree of precision may attain to ± 0·1 c.c. of the ferrous solution, *i.e.* to ± 0·000001 grm. of iron per 5 c.c. of solution tested, provided these 5 c.c. do not contain more than 0·00002 grm. of iron.

VII. *Free Sulphuric Acid.*—The presence of this acid may be tested by campeachy wood tincture (1 part of wood, 3 of water, and 1 of alcohol), the violet tinge of which is changed to brown. The estimation is a delicate operation.

(1) *Determination in an Alcoholic Extract.*—According to O. Miller (*Zeits. Anal. Chem.*, vol. 24, p. 258), the extract prepared by treating the substance with alcohol is evaporated to expel the latter, and titrated with $\frac{1}{10}$-normal soda in presence of methyl orange. According to Williams, the idea of expelling the alcohol must be abandoned, in order to avoid loss of H_2SO_4, the acidity being then titrated with NaHO in presence of phenolphthalein as indicator.

In the former case, according to Lunge, the results are too low, and in the latter too high, besides being irregular.

(2) *Estimation by Boiling with an Excess of Ammonium-magnesum Phosphate.*—According to Erlenmeyer and Levinstein, the whole of the Al_2O_3 is precipitated as a neutral salt, and the free H_2SO_4 can be determined in the filtered liquid. Beilstein and Grosset, however, do not recommend this method, preferring the following, based on the fact that when neutral ammonium sulphate is added to aluminium sulphate the latter is precipitated as alum, leaving the free sulphuric acid in solution. The remainder of the alum and the excess of ammonium sulphate are precipitated by alcohol.

1 or 2 grms. of aluminium sulphate are dissolved in 5 c.c. of water, the solution being treated with 5 c.c. of a saturated solution of $(NH_4)_2SO_4$, then shaken up frequently during $\frac{1}{4}$ hour, and afterwards treated with 50 c.c. of 95 per cent. alcohol. After filtration and washing with 50 c.c. of alcohol the filtrate and washings are evaporated on the water bath, taken up with water, and titrated with $\frac{1}{10}$-normal soda in presence of phenolphthalein.

Lunge regards this method as the most exact.

The method consisting in the direct titration of the substance with tropeolin 00, methyl orange, etc., is inaccurate (H. de Kéler and G. Lunge, *Monit. Scient.*, 1896, p. 40).

CHAPTER VIII

IRON

§ I. ANALYTICAL CHARACTERISTICS OF IRON SALTS

169. **General Reactions of the Iron Salts.**—*A.* FERROUS SALTS.—These salts are generally pale green when hydrated, white when anhydrous. They are thrown down from solution, by potash or soda, as a white precipitate, turning green, and finally brown, and insoluble in an excess of the reagent. Owing to the influence of the air it is difficult to obtain the precipitate quite white, unless the experiment is made in a glass through which a current of carbon dioxide is passed for several minutes. A similar precipitate, insoluble in excess, is also furnished by ammonia.

An alkali carbonate, poured into a solution of a ferrous salt, gives a white precipitate of carbonate, of low stability, which rapidly parts with CO_2 and undergoes the same transformations as the hydroxide.

Sulphuretted hydrogen gives no precipitate with ferrous salts so long as they are acid, but ammonium sulphide gives a black precipitate, insoluble in excess.

Oxalic acid and the soluble oxalates furnish a yellow precipitate of ferrous oxalate, unalterable in air, and soluble in acids.

Yellow prussiate of potash (potassium ferrocyanide) gives a white precipitate, turning blue in air..

Red prussiate (potassium ferricyanide) gives a very deep blue and highly characteristic precipitate.

Ammonium succinate and benzoate give no precipitate; neither does tannin, though in this case the liquid turns black directly on exposure to the air.

Potassium phosphate gives a white precipitate, turning to blue; and the arsenate a white precipitate, which turns green.

B. FERRIC SALTS.—These are obtained by the oxidation of ferrous salts, or by dissolving ferric hydroxide in acids. They are deep yellow or red-brown in colour.

The alkalis, potash, soda, and ammonia give a brown precipitate of ferric hydroxide, insoluble in an excess of the reagent.

The alkali carbonates give the same brown precipitate of hydroxide, CO_2 being liberated.

Sulphuretted hydrogen gives a finely divided white precipitate of sulphur, the ferric salt being at the same time reduced to the ferrous state—

$$Fe_2Cl_6 + H_2S = 2HCl + S + 2FeCl_2,$$
$$Fe_2(SO_4)_3 + H_2S = H_2SO_4 + S + 2FeSO_4.$$

Barium carbonate is able to throw down ferric oxide even in the cold, CO_2 being disengaged, and the barium displacing iron in the solution.

Potassium ferrocyanide gives a deep blue precipitate, whilst the ferricyanide does not produce any. These reagents enable the ferrous salts to be distinguished from the ferric salts.

In neutral or ammoniacal solutions a brown precipitate is produced by ammonium succinate or benzoate.

Tannin gives a bluish-black precipitate of ordinary ink; and potassium thiocyanate turns ferric salts a blood-red colour.

The presence of organic matter in the solution prevents precipitation by ammonia or potash, but ammonium sulphide will always throw down the whole of the iron as an insoluble sulphide.

When, as often happens, ferrous and ferric salts are present together, the mixture may be tested with sulphuretted hydrogen, which, in presence of a ferric salt, will give a white deposit of sulphur. Another portion of the solution may then be tested with potassium ferricyanide, a deep blue precipitate indicating that a ferrous salt is also present.

170. **Estimation of Iron.**—This may be effected by gravimetric, volumetric, or colorimetric methods. The last-named

having been already described in the analysis of aluminium sulphate, need not be further discussed now.

For gravimetric determinations the whole of the iron is peroxidised by means of HNO_3, chlorine, *aqua regia*, bromine, etc. On boiling the liquid and adding NH_3, the iron comes down as hydroxide, which is collected, decanted, and washed until free from all soluble salts; after which it is dried and removed from the filter, the latter being then calcined separately. To counteract any reduction of the iron adhering to the filter by the carbon formed during calcination, the residue is treated with a little HNO_3, then evaporated, calcined afresh, and united to the main precipitate, which is afterwards calcined, cooled, and weighed.

If the iron is in the condition of nitrate, this method is very accurate; but if in the state of chloride, the precipitate will have to be washed until the washings cease to react in presence of silver nitrate. In the absence of this precaution volatile ferric chloride will be formed during calcination, and will falsify the results.

When the iron cannot be isolated by NH_3—as, for instance, in presence of citric acid, tartaric acid, or other organic bodies—ammonium sulphide is employed as precipitant, the iron sulphide being collected, washed, calcined, and weighed. The results will be accurate, provided the amount of sulphide is small; otherwise the calcination residue must be taken up with HCl and re-precipitated with ammonia.

The method most generally used, however, is the Marguerite titrimetic method, based on the action of potassium permanganate. This salt oxidises ferrous salts in dilute acid solutions, and converts them into ferric salts, being itself decolorised and broken up into salts of manganese and potassium.

When the reaction is complete, the end point is shown by the persistent rose-red coloration produced by a single drop of the reagent in excess—

$$10FeSO_4 + 8H_2SO_4 + K_2Mn_2O_8$$
$$= 5[Fe_2(SO_4)_3] + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

The reagent employed is a solution containing 4 to 5 grms.

of pure crystallised permanganate per litre. This is run into a burette graduated in cubic mm., and is standardised to ascertain the volume required to peroxidise a given weight of iron.

For this purpose about 3 to 4 dgrms. of very pure iron wire, in small fragments, are dissolved by heat in a 100 c.c. flask containing water and 5 to 6 grms. of H_2SO_4. Ferrous sulphate is formed and hydrogen liberated, the latter escaping through a tube traversing the cork. When all the metal is dissolved the solution is placed in a porcelain capsule, the flask washed with cold distilled water, and the whole made up to 300–400 c.c. The permanganate is then run in from the burette, with constant stirring; the red drops disappear rapidly at first, and the hitherto colourless liquid turns yellow owing to the conversion of the ferrous sulphate into the ferric state. Soon the reaction becomes slower, and the permanganate must be added with care so as to enable the operator to judge at which drop the red coloration becomes permanent despite the stirring. The volume consumed is then read off and calculated to unity, *i.e.* to 1 grm. of iron.

This being done, $\frac{1}{2}$ to 1 grm. of the substance under examination (according to the presumed richness in iron) is dissolved in boiling HCl and evaporated with 5 to 6 grms. of H_2SO_4 until white fumes begin to appear, whereupon the mass is cooled and taken up with water. The resulting solution generally contains the iron as ferric sulphate, and has to be reduced to the ferrous state before the permanganate can react. This conversion is best effected by adding granulated zinc, the nascent hydrogen thereupon liberated reducing the iron salt. As soon as the liquid becomes decolorised it is transferred to a white capsule, and acidified if necessary, after which it is diluted, and titrated as already described.

Provided the above conditions be strictly maintained, this method is very accurate; but it is only suitable for cases where the iron alone has to be estimated.

In place of metallic iron, which always contains 0·3 to 0·4 per cent. of carbon and other impurities, the double sulphate of iron and ammonium—

$$FeSO_4 + (NH_4)_2SO_4 + 6H_2O$$

—is employed for standardising the permanganate reagent. This sulphate is obtainable pure, keeps without changing, and, as it contains just $\frac{1}{7}$ of its own weight of iron, all that is necessary for the rapid standardising of the permanganate is to dissolve 2 to 2·5 grms. of the sulphate in 300 to 400 c.c. of pure cold water and 5 to 6 grms. of free sulphuric acid.

171. **Separation of Iron from other Metals.**—To separate iron from the alkali metals, it is peroxidised and thrown down by ammonia. The filtrate and washings are united, and calcined to drive off ammonium salts, the alkali metals being left in the residue.

When barium and strontium are present the same treatment is applied, except that the iron oxide precipitate should be re-dissolved and re-precipitated if there is any risk that it has carried down traces of these alkaline earths. If, on the other hand, the latter are first thrown down by sulphuric acid, a good deal of the iron is carried away and cannot be entirely recovered, even by washing in boiling concentrated HCl. The same applies when calcium and magnesium are present, provided there be an excess of ammonium salts in the solution. In such event the method based on the decomposition of the nitrates—already indicated in the case of aluminium and calcium—may be utilised to advantage. The iron remains in the state of peroxide, insoluble in ammonium nitrate, whilst the lime and magnesia are entirely dissolved.

To determine iron in presence of aluminium, they are precipitated together by ammonium sulphide, then calcined, oxidised by nitric acid, heated again and weighed, after which they are re-dissolved in HCl, evaporated with H_2SO_4, and the iron titrated with permanganate.

Another method consists in reducing the mixture of the two oxides by hydrogen at red heat and taking up the residue with very dilute nitric acid, which dissolves out the iron alone. This treatment is also applicable in presence of chromium oxide.

Iron can also be separated from manganese, cobalt, nickel, etc., by precipitation as peroxide by barium carbonate out of contact with air.

Finally, when iron peroxide, alumina, manganese oxide, cobalt oxide, etc., are present in the same solution, the usual mode of analysis is to throw down the iron and aluminium as acetates. The hydrochloric acid solution is greatly diluted, and saturated with sodium carbonate until the liquid turns red and loses its transparence, whereupon it is treated with an excess of sodium acetate and boiled. The iron and alumina separate as insoluble basic acetates, leaving a clear, colourless solution. The precipitate is collected with the usual precautions and calcined, the resulting oxides being weighed. The manganese will be found in the filtrate, and can be thrown down by bromine or ammonium sulphide.

All the metals precipitable by sulphuretted hydrogen in acid solutions are readily separated from iron by this reagent.

§ 2. ANALYSIS OF CERTAIN FERRUGINOUS PRODUCTS

172. **Analysis of Pyritic Lignite.**—The substances to be estimated are: moisture, insoluble matter, ferrous sulphate, ferric sulphate, aluminium sulphate, total H_2SO_4, iron disulphide.

I. *Moisture.*—A portion of the sample is finely powdered, and 2 grms. are then dried at 100° C. until of constant weight.

II. *Insoluble Matter.*—Another 2 grms. are treated for this purpose, and washed with hot water as quickly as possible in order to prevent oxidation of the sulphide. The clear liquids are united and made up to a definite volume, the residue being dried and weighed.

III. *Ferrous Sulphate.*—This is titrated with permanganate on an aliquot portion of the solution. Owing to the presence of organic matter, which decolorises the permanganate after all the iron has been oxidised, the end point is not well defined. For its better detection a few drops of the solution are taken at intervals and tested with ferricyanide, the absence of the characteristic blue precipitate indicating complete oxidation of the iron. The result is calculated in terms of ferrous sulphate.

IV. *Ferric Sulphate.*—A portion of the liquid is reduced by means of zinc, and then titrated with permanganate. The difference between this result and that of the preceding test gives the amount of iron in the ferric state, and from this the quantity of ferric sulphate is calculated.

V. *Aluminium Sulphate* is determined by precipitation with sodium thiosulphate.

VI. *Total Sulphuric Acid.*—A portion of the clear solution is acidified by HCl and precipitated with barium chloride, the barium sulphate being collected with the usual precautions.

VII. *Iron Disulphide.*—One grm. of the very finely powdered substance is treated with *aqua regia* on the sand bath at moderate heat, the acid being renewed as evaporation progresses. Finally, greater heat is employed, a few crystals of potassium chlorate being added from time to time. Under these conditions the sulphur is oxidised to sulphuric acid. After the excess of nitric acid has been expelled by heat the mass is taken up with water, filtered, and washed, a portion of the solution being tested to determine the sulphuric acid present. On deducting the figures from the preceding test, the remainder gives the sulphuric acid corresponding to the unoxidised sulphur in the substance. This is then calculated to iron disulphide.

173. **Analysis of Ferrous Sulphate.**—As a rule the iron alone is estimated, in the form of ferrous sulphate, by simply dissolving the salt, acidifying with H_2SO_4, and titrating with permanganate. If the insoluble matter—ferric sulphate, total H_2SO_4, etc.—are also to be determined, this is done by the methods already described.

174. **Analysis of Ferric Sulphate.**—Substances to be determined: moisture, insoluble residue, soluble ferric sulphate, soluble H_2SO_4, free H_2SO_4.

I. *Moisture.*—Five grms. are dried in the oven till constant.

II. *Insoluble Residue.*—Five grms. are extracted with hot distilled water, the residue being washed until the liquid ceases to give a precipitate with barium chloride. This residue is dried and weighed.

III. *Soluble Ferric Sulphate* is estimated by titration with permanganate after the reduction of a portion of the above solution by means of zinc.

IV. *Soluble* H_2SO_4.—An aliquot part of the solution is acidified with HCl. The iron is then thrown down by ammonia, and is washed, dried, and weighed. The weight should correspond to that of the ferric sulphate. In case of difference, search must be made for alumina, lime, etc.

The clear liquid, acidified by HCl, is used to estimate the H_2SO_4 by means of barium chloride.

V. *Free* H_2SO_4 is ascertained in an approximate manner by deducting the combined H_2SO_4 from the total.

175. **Analysis of Rouil Mordant.**—The estimation usually includes sulphuric acid, ferrous sulphate, total iron, and soda.

I. *Sulphuric Acid.*—This is estimated by means of barium chloride after the iron has been thrown down by ammonia, or even before such precipitation. In the latter event the results are accurate enough for practical purposes, even though a little iron be carried down by the precipitate. In either event the solution must be acidified with HCl before the barium chloride is added.

II. *Ferrous Sulphate* is readily estimated by the permanganate method, 10 c.c. being made up to 100 c.c., then strongly acidified with H_2SO_4, and titrated until a permanent rose-red tint appears.

III. *Total Iron.*—Some precaution is necessary owing to the almost invariable presence of small quantities of nitrous products, free HNO_3, etc., which bodies are also reduced by zinc and falsify the results by their influence on the permanganate. To remove or destroy them, 10 c.c. of the substance are boiled with 2 to 3 c.c. of H_2SO_4, and evaporated to near dryness. The mass is then taken up with water, reduced with zinc, and titrated in the usual manner, the result giving the total iron.

IV. *Soda.*—This may be estimated as chloride after the metals and H_2SO_4 have been removed. This method is, however, cumbrous, and may be replaced by the following, which gives results near enough to show the quality of the substance.

Ten c.c. of the *Rouil* liquor are treated with an excess of normal soda, a note being taken of the quantity used. The liquid and precipitate are then made up to 500 c.c., shaken, and filtered. 100 to 200 c.c. of the filtrate (= 1 or 2 c.c. of original liquor) are collected, and the excess of soda titrated with normal sulphuric acid, the difference giving the amount of H_2SO_4 relating to the bases precipitable by soda. On deducting this from the total H_2SO_4, the remainder is calculated to sodium bisulphate.

FINIS

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VEGETABLE FATS AND OILS: Their Practical Preparation, Purification and Employment for Various Purposes, their Properties, Adulteration and Examination. A Handbook for Oil Manufacturers and Refiners, Candle, Soap and Lubricating Oil Makers, and the Oil and Fat Industry in General. Translated from the German of Louis Edgar Andés. With Ninety-four Illustrations. 320 pp. 1897. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net, post free.

Contents.

Statistical Data. General Properties of the Vegetable Fats and Oils. Estimation of the Amount of Oil in Seeds. Table of Vegetable Fats and Oils, with French and German Nomenclature, Source and Origin and Percentage of Fat in the Plants from which they are Derived. The Preparation of Vegetable Fats and Oils: Storing Oil Seeds; Cleaning the Seed. Apparatus for Grinding Oil Seeds and Fruits. Installation of Oil and Fat Works. Extraction Method of Obtaining Oils and Fats. Oil Extraction Installations. Press Moulds. Non-drying Vegetable Oils. Vegetable drying Oils. Solid Vegetable Fats. Fruits Yielding Oils and Fats. Wool-softening Oils. Soluble Oils. Treatment of the Oil after Leaving the Press Improved Methods of Refining with Sulphuric Acid and Zinc Oxide or Lead Oxide. Refining with Caustic Alkalies, Ammonia, Carbonates of the Alkalies, Lime. Bleaching Fats and Oils. Practical Experiments on the Treatment of Oils with regard to Refining and Bleaching. Testing Oils and Fats.

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IRON-CORROSION, ANTI-FOULING AND ANTI-CORROSIVE PAINTS. By Louis Edgar Andés. Sixty-two Illustrations. 275 pp. Translated from the German. 1900. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net, post free.

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Part IV., **Chemical Characteristics of Iron and Aluminium.—Analysis of Various Aluminous or Ferruginous Products.**—Chapter VII., Aluminium.

LUBRICATING OILS, FATS AND GREASES: Their Origin, Preparation, Properties, Uses and Analyses. A Handbook for Oil Manufacturers, Refiners and Merchants, and the Oil and Fat Industry in General. By GEORGE H. HURST, F.C.S. Sixty-five Illustrations. 313 pp. 1896. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net, post free.

Contents.

Chapters I., **Introductory.** Oils and Fats, Fatty Oils and Fats, Hydrocarbon Oils, Uses of Oils.—II., **Hydrocarbon Oils.** Distillation, Simple Distillation, Destructive Distillation, Products of Distillation, Hydrocarbons, Paraffins, Olefins, Napthenes.—III., **Scotch Shale Oils.** Scotch Shales, Distillation of Scotch Oils, Shale Retorts, Products of Distilling Shales, Separating Products, Treating Crude Shale Oil, Refining Shale Oil, Shale Oil Stills, Shale Naphtha Burning Oils, Lubricating Oils, Wax.—IV., **Petroleum.** Occurrence, Geology, Origin, Composition, Extraction, Refining, Petroleum Stills, Petroleum Products, Cylinder Oils, Russian Petroleum, Deblooming Mineral Oils.—V., **Vegetable and Animal Oils.** Introduction, Chemical Composition of Oils and Fats, Fatty Acids, Glycerine, Extraction of Animal and Vegetable Fats and Oils, Animal Oils, Vegetable Oils, Rendering, Pressing, Refining, Bleaching, Tallow, Tallow Oil, Lard Oil, Neatsfoot Oil, Palm Oil, Palm Nut Oil, Cocoanut Oil, Castor Oil, Olive Oil, Rape and Colza Oils, Arachis Oil, Niger Seed Oil, Sperm Oils, Whale Oil, Seal Oil, Brown Oils, Lardine, Thickened Rape Oil.—VI., **Testing and Adulteration of Oils.** Specific Gravity, Alkali Tests, Sulphuric Acid Tests, Free Acids in Oils, Viscosity Tests, Flash and Fire Tests, Evaporation Tests, Iodine and Bromide Tests, Elaidin Test, Melting Point of Fat, Testing Machines.—VII., **Lubricating Greases.** Rosin Oil, Anthracene Oil, Making Greases, Testing and Analysis of Greases.—VIII., **Lubrication.** Friction and Lubrication, Lubricant, Lubrication of Ordinary Machinery, Spontaneous Combustion of Oils, Stainless Oils, Lubrication of Engine Cylinders, Cylinder Oils.—**Appendices.** A. Table of Baume's Hydrometer—B. Table of Thermometric Degrees—C. Table of Specific Gravities of Oils—**Index.**

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"23*rd May*, 1899"

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By Ernest J. Parry, B.Sc. (Lond.), F.I.C., F.C.S. Illustrated with Twenty Engravings. 400 pp. 1899. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net, post free.

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DRYING OILS, BOILED OIL AND SOLID AND LIQUID DRIERS.

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Contents.

Chapters I., General Chemical and Physical Properties of the Drying Oils; Cause of the Drying Property; Absorption of Oxygen; Behaviour towards Metallic Oxides, etc.—II., The Properties of and Methods for obtaining the Drying Oils.—III., Production of the Drying Oils by Expression and Extraction; Refining and Bleaching; Oil Cakes and Meal; The Refining and Bleaching of the Drying Oils; The Bleaching of Linseed Oil.—IV., The Manufacture of Boiled Oil; The Preparation of Drying Oils for Use in the Grinding of Paints and Artists' Colours and in the Manufacture of Varnishes by Heating over a Fire or by Steam, by the Cold Process, by the Action of Air, and by Means of the Electric Current; The Driers used in Boiling Linseed Oil; The Manufacture of Boiled Oil and the Apparatus therefor; Livache's Process for Preparing a Good Drying Oil and its Practical Application.—V., The Preparation of Varnishes for Letterpress, Lithographic and Copperplate Printing, for Oilcloth and Waterproof Fabrics; The Manufacture of Thickened Linseed Oil, Burnt Oil, Stand Oil by Fire Heat, Superheated Steam, and by a Current of Air.—VI., Behaviour of the Drying Oils and Boiled Oils towards Atmospheric Influences, Water, Acids and Alkalies.—VII., Boiled Oil Substitutes.—VIII., The Manufacture of Solid and Liquid Driers from Linseed Oil and Rosin; Linolic Acid Compounds of the Driers.—IX., The Adulteration and Examination of the Drying Oils and Boiled Oil.

GLUE AND GLUE TESTING.

By Samuel Rideal, D.Sc. Lond., F.I.C. Fourteen Engravings. 144 pp. 1900. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net, post free.

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TECHNOLOGY OF PETROLEUM: Oil Fields of the World—Their History, Geography and Geology—Annual Production and Development—Oil-well Drilling—Transport. By Henry Neuberger and Henry Noalhat. Translated from the French by J. G. McIntosh. 540 pp. Illustrations, Maps and Plates. [*In the Press.*

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I., **Behaviour of the Paper Fibres during the Process of Dyeing, Theory of the Mordant**—Cotton; Flax and Hemp; Esparto; Jute; Straw Cellulose; Chemical and Mechanical Wood Pulp; Mixed Fibres; Theory of Dyeing.—II., **Colour Fixing Mediums (Mordants)**—Alum; Aluminium Sulphate; Aluminium Acetate; Tin Crystals (Stannous Chloride); Copperas (Ferrous Sulphate); Nitrate of Iron (Ferric Sulphate); Pyrolignite of Iron (Acetate of Iron); Action of Tannic Acid; Importance of Materials containing Tannin; Treatment with Tannic Acid of Paper Pulp intended for dyeing; Blue Stone (Copper Sulphate); Potassium Bichromate; Sodium Bichromate; Chalk (Calcium Carbonate); Soda Crystals (Sodium Carbonate); Antimony Potassium Tartrate (Tartar Emetic).—III., **Influence of the Quality of the Water Used.**—IV., **Inorganic Colours**—1. Artificial Mineral Colours: Iron Buff; Manganese Bronze; Chrome Yellow (Chromate of Lead); Chrome Orange (Basic Chromate of Lead); Red Lead; Chrome Green; Blue with Yellow Prussiate; Prussian Blue; Method for Producing Prussian Blue free from Acid; Ultramarine—2. Natural Mineral Colours (Earth Colours): Yellow Earth Colours; Red Earth Colours; Brown Earth Colours; Green, Grey and Black Earth Colours; White Earth Colours; White Clay (China Clay); White Gypsum; Baryta; Magnesium Carbonate; Talc, Soapstone.—V., **Organic Colours**—1. Colours of Vegetable and Animal Origin: (*a*) *Substantive* (*Direct Dyeing*) *Colouring Matters:* Annatto; Turmeric; Safflower; (*b*) *Adjective* (*Indirect Dyeing*) *Colouring Matters:* Redwood; Cochineal; Weld; Persian Berries; Fustic Extract; Quercitron; Catechu (Cutch); Logwood Extract—2. Artificial Organic (Coal Tar) Colours: Acid Colours; Basic Colours; Substantive (Direct Dyeing) Colours; Dissolving of the Coal Tar Colours; Auramine°°; Naphthol Yellow S°; Quinoline Yellow°; Metanil Yellow°; Paper Yellow°; Azoflavine RS°, S°; Cotton Yellow Gxx and Rxx; Orange II°; Chrysoïdine A°°, RL°°; Vesuvine Extra°°; Vesuvine BC°°; Fast Brown°, Naphthylamine Brown°; Water Blue IN°; Water Blue TB°; Victoria Blue B°°; Methylene Blue MD°°; Nile Blue R°°; New Blue S°°; Indoïne Blue BB°°; Eosine 442 Nx; Phloxine BBN; Rhodamine B°°; Rhodamine 6 G°°; Naphthylamine Red G°; Fast Red A°; Cotton Scarlet°; Erythrine RR°; Erythrine X°; Erythrine P°; Ponceau 2 R°; Fast Ponceau G° and B°; Paper Scarlet P°°; Saffranine PP°°; Magenta Powder A°°; Acetate of Magenta°°; Cerise D 10°°; Methyl Violet BB°°; Crystal Violet°°; Acid Violet 3 BN°, 4 R°; Diamond Green B°°; Nigrosine WL°; Coal Black°°; Brilliant Black B°.—VI., **Practical Application of the Coal Tar Colours according to their Properties and their Behaviour towards the Different Paper Fibres**—Coal Tar Colours, which rank foremost, as far as their fastness to light is concerned; Colour Combinations with which colourless or nearly colourless Backwater is obtained; Colours which do not bleed into White Fibres, for Blotting and Copying Paper Pulp; Colours which produce the best results on Mechanical Wood and on Unbleached Sulphite Wood; Dyeing of Cotton, Jute and Wool Half-stuff for Mottling White or Light Coloured Papers; Colours suitable for Cotton; Colours specially suitable for Jute Dyeing; Colours suitable for Wool Fibres.—VII., **Dyed Patterns on Various Pulp Mixtures**—Placard and Wrapping Papers; Black Wrapping and Cartridge Papers; Blotting Papers; Mottled and Marbled Papers made with Coloured Linen, Cotton and Union Rags, or with Cotton, Jute, Wool and Sulphite Wood Fibres, dyed specially for this purpose; Mottling with Dark Blue Linen; Mottling with Dark Blue Linen and Dark Blue Cotton; Mottling with Dark Blue Cotton; Mottling with Dark Blue and Red Cotton; Mottling with Dark Red Cotton; Mottling of Bleached Stuff, with 3 to 4 per cent. of Dyed Cotton Fibres; Mottling with Dark Blue Union (Linen and Wool or Cotton Warp with Wool Weft); Mottling with Blue Striped Red Union; Mottling of Bleached Stuff with 3 to 4 per cent. of Dyed Wool Fibres; Mottling of Bleached Stuff with 3 to 4 per cent. of Dyed Jute Fibres; Mottling of Bleached Stuff with 3 to 4 per cent. of Dyed Sulphite Wood Fibres; Wall Papers; Packing Papers.—VIII., **Dyeing to Shade**—Index.

Press Opinion.

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Enamelling on Metal.

ENAMELS AND ENAMELLING. An Introduction to the Preparation and Application of all Kinds of Enamels for Technical and Artistic Purposes. For Enamel Makers, Workers in Gold and Silver, and Manufacturers of Objects of Art. By Paul Randau. Translated from the German. With Sixteen Illustrations. 180 pp. 1900. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net, post free.

Contents.

I., Introduction.—II., Composition and Properties of Glass.—III., Raw Materials for the Manufacture of Enamels.—IV., Substances Added to Produce Opacity.—V., Fluxes.—VI., Pigments.—VII., Decolorising Agents.—VIII., Testing the Raw Materials with the Blow-pipe Flame.—IX., Subsidiary Materials.—X., Preparing the Materials for Enamel Making.—XI., Mixing the Materials.—XII., The Preparation of Technical Enamels, The Enamel Mass.—XIII., Appliances for Smelting the Enamel Mass.—XIV., Smelting the Charge.—XV., Composition of Enamel Masses.—XVI., Composition of Masses for Ground Enamels.—XVII., Composition of Cover Enamels.—XVIII., Preparing the Articles for Enamelling.—XIX., Applying the Enamel.—XX., Firing the Ground Enamel.—XXI., Applying and Firing the Cover Enamel or Glaze.—XXII., Repairing Defects in Enamelled Ware.—XXIII., Enamelling Articles of Sheet Metal.—XXIV., Decorating Enamelled Ware.—XXV., Specialities in Enamelling.—XXVI., Dial-plate Enamelling.—XXVII., Enamels for Artistic Purposes, Recipes for Enamels of Various Colours.—Index.

Press Opinions.

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THE ART OF ENAMELLING ON METAL. By W. Norman Brown. Twenty-eight Illustrations. 60 pp. 1900. Price 2s. 6d.; Abroad, 3s.; strictly net, post free.

Contents.

Chapters I., History—Cloisonnė—Champs Levė—Translucent Enamel—Surface Painted Enamels.—II., Cloisonnė—Champs Levės—Translucent—Painted.—III., Painted Enamel—Apparatus—Furnaces and Muffles for Firing.—IV., The Copper Base or Plate—Planishing—Cloisons—Champ Levė Plates.—V., Enamels—Trituration—Washing—Coating a Plate with Enamel—Firing Ordinary Plaques for Painting—Designing—Squaring off.—VI., Designs for Cloisonnė—Designs for Painted Enamels—Technical Processes—Brushes, etc.,—Colours—Grisaille—Full-coloured Designs.

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Books on Textile and Dyeing Subjects.

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Yarn Testing. III., **Determining the Yarn Number.**—IV., **Testing the Length of Yarns.**—V., **Examination of the External Appearance of Yarn.**—VI., **Determining the Twist of Yarn and Twist.**—VII., **Determination of Tensile Strength and Elasticity.**—VIII., **Estimating the Percentage of Fat in Yarn.**—IX., **Determination of Moisture** (Conditioning).—**Appendix.**

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DECORATIVE AND FANCY TEXTILE FABRICS. With Designs and Illustrations. By R. T. LORD. A Valuable Book for Manufacturers and Designers of Carpets, Damask, Dress and all Textile Fabrics. 200 pp. 1898. 132 Designs and Illustrations. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net, post free.

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"The book under notice is intended as an instructor to those engaged in power-loom weaving, and, judging by its compilation, the author is a thorough master of the craft. It is not overloaded with details, and he manages to compress in a book of some 150 pages all that one can possibly wish to know about the different parts of the machinery, whether of English or foreign make, and for whatever kind of cloth required. A comprehensive summary is also included of the various yarns and methods of numbering them, as well as a few useful hints and a number of coloured diagrams for mandarin weavings. The book is printed in bold, legible type, on good paper, has a copious index, and is well and strongly bound."—*Ashton-under-Lyne Herald.*

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COLOUR: A HANDBOOK OF THE THEORY OF COLOUR. By George H. Hurst, F.C.S. With Ten Coloured Plates and Seventy-two Illustrations. 160 pp. 1900. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net, post free.

Contents.

Chapters I., **Colour and Its Production**. Light, Colour, Dispersion of White Light Methods of Producing the Spectrum, Glass Prism and Diffraction Grating Spectroscopes, The Spectrum, Wave Motion of Light, Recomposition of White Light, Hue, Luminosity, Purity of Colours, The Polariscope, Phosphorescence, Fluorescence, Interference.—II., **Cause of Colour in Coloured Bodies.** Transmitted Colours, Absorption Spectra of Colouring Matters.—III., **Colour Phenomena and Theories.** Mixing Colours, White Light from Coloured Lights, Effect of Coloured Light on Colours, Complementary Colours, Young-Helmholtz Theory, Brewster Theory, Supplementary Colours, Maxwell's Theory, Colour Photography.—IV., **The Physiology of Light.** Structure of the Eye, Persistence of Vision, Subjective Colour Phenomena, Colour Blindness.—V., **Contrast.** Contrast, Simultaneous Contrast, Successive Contrast, Contrast of Tone, Contrast of Colours, Modification of Colours by Contrast, Colour Contrast in Decorative Design.—VI., **Colour in Decoration and Design.** Colour Harmonies, Colour Equivalents, Illumination and Colour, Colour and Textile Fabrics, Surface Structure and Colour.—VII., **Measurement of Colour.** Colour Patch Method, The Tintometer, Chromometer.

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THE COLOUR PRINTING OF CARPET YARNS. A Useful Manual for Colour Chemists and Textile Printers. By David Paterson, F.C.S. Seventeen Illustrations. 132 pp. 1900. Price 7s. 6d.; India and Colonies, 8s. Other Countries, 8s. 6d.; strictly net, post free.

Contents.

Chapters I., Structure and Constitution of Wool Fibre.—II., Yarn Scouring.—III., Scouring Materials.—IV., Water for Scouring.—V., Bleaching Carpet Yarns.—VI., Colour Making for Yarn Printing.—VII., Colour Printing Pastes.—VIII., Colour Recipes for Yarn Printing.—IX., Science of Colour Mixing.—X., Matching of Colours.—XI., "Hank" Printing.—XII., Printing Tapestry Carpet Yarns.—XIII., Yarn Printing.—XIV., Steaming Printed Yarns.—XV., Washing of Steamed Yarns.—XVI., Aniline Colours Suitable for Yarn Printing.—XVII., Glossary of Dyes and Dye-wares used in Wood Yarn Printing.—Appendix.

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A PRACTICAL TREATISE ON THE BLEACHING OF LINEN AND COTTON YARN AND FABRICS.

By L. Tailfer, Chemical and Mechanical Engineer. Translated from the French by John Geddes McIntosh, Lecturer on Chemical Technology, London. 1901. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net, post free.

Contents.

Chapter I. General Considerations on Bleaching. Chapter II. Steeping. Chapter III Washing: Its End and Importance—Roller Washing Machines—Wash Wheel (Dash Wheel)—Stocks or Wash Mill—Squeezing. Chapter IV. Lye Boiling—Lye Boiling with Milk of Lime—Lye Boiling with Soda Lyes—Description of Lye Boiling Keirs—Operations of Lye Boiling—Concentration of Lyes. Chapter V. Mather and Platt's Keir—Description of the Keir—Saturation of the Fabrics—Alkali used in Lye Boiling—Examples of Processes. Chapter VI. Soap—Action of Soap in Bleaching—Quality and Quantity of Soaps to use in the Lye—Soap Lyes or Scalds—Soap Scouring Stocks. Chapter VII. Bleaching on Grass or on the Bleaching Green or Lawn. Chapter VIII. Chemicking—Remarks on Chlorides and their Decolourising Action—Chemicking Cisterns—Chemicking—Strengths, etc. Chapter IX. Sours—Properties of the Acids—Effects Produced by Acids—Souring Cisterns. Chapter X. Drying—Drying by Steam—Drying by Hot Air—Drying by Air. Chapter XI. Damages to Fabrics in Bleaching—Yarn Mildew—Fermentation—Iron Rust Spots—Spots from Contact with Wood—Spots incurred on the Bleaching Green—Damages arising from the Machines. Chapter XII. Examples of Methods used in Bleaching—Linen—Cotton. Chapter XIII. The Valuation of Caustic and Carbonated Alkali (Soda) and General Information Regarding these Bodies—Object of Alkalimetry—Titration of Carbonate of Soda—Comparative Table of Different Degrees of Alkalimetrical Strength—Five Problems relative to Carbonate of Soda—Caustic Soda, its Properties and Uses—Mixtures of Carbonated and Caustic Alkali—Note on a Process of Manufacturing Caustic Soda and Mixtures of Caustic and Carbonated Alkali (Soda). Chapter XIV. Chlorometry—Titration—Wagner's Chlorometric Method—Preparation of Standard Solutions—Apparatus for Chlorine Valuation—Alkali in Excess in Decolourising Chlorides. Chapter XV. Chlorine and Decolourising Chlorides—Synopsis—Chlorine—Chloride of Lime—Hypochlorite of Soda—Brochoki's Chlorozone—Various Decolourising Hypochlorites—Comparison of Chloride of Lime and Hypochlorite of Soda. Chapter XVI. Water—Qualities of Water—Hardness—Dervaux's Purifier—Testing the Purified Water—Different Plant for Purification—Filters. Chapter XVII. Bleaching of Yarn—Weight of Yarn—Lye Boiling—Chemicking—Washing—Bleaching of Cotton Yarn. Chapter XVIII. The Installation of a Bleach Works—Water Supply—Steam Boilers—Steam Distribution Pipes—Engines—Keirs—Washing Machines—Stocks—Wash Wheels—Chemicking and Souring Cisterns—Various—Buildings. Chapter XIX. Addenda—Energy of Decolourising Chlorides and Bleaching by Electricity and Ozone—Energy of Decolourising Chlorides—Chlorides—Production of Chlorine and Hypochlorites by Electrolysis—Lunge's Process for increasing the intensity of the Bleaching Power of Chloride of Lime—Trilfer's Process for Removing the Excess of Lime or Soda from Decolourising Chlorides—Bleaching by Ozone.

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