Circular 58

Economic Recovery of Selenium

by Flotation From Sandstone Ores

of New Mexico

by Roshan B. Bhappu

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FROM SANDSTONE ORES OF NEW MEXICO

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1961

STATE BUREAU OF MINES & MINERAL RESOURCES NEW
MEXICO INSTITUTE OF MINING & TECHNOLOGY

CAMPUS STATION   SOCORRO, NEW MEXICO

CONTENTS

ILLUSTRATIONS

ABSTRACT

Investigation has shown that the selenium-bearing sandstone ores from the Morrison and Galisteo formations of New Mexico are amenable to simple froth-flotation procedures. The common flotation reagents used are soda ash, sodium silicate, a neutral oil (kerosene), a xanthate, and a frother. Conditioning of the pulp prior to flotation plays an important role in the process, especially if the sandstone contains excessive amounts of slimy clays and shale s.

Under optimum conditions, the selenium flotation is rapid and selective; selenium recovery above 85 percent is possible; and an acceptable grade of concentrates above 4 percent is obtainable.

From the economic viewpoint, flotation recovery of selenium appears attractive. The cutoff grades for the profitable recovery of selenium as the major ore constituent are 0.12 and 0. 04 percent for underground and open-pit mining operations respectively. On the other hand, when selenium is recovered as a byproduct of some other mining operation, such as mining for uranium, the cutoff grade is only 0. 01 percent.

INTRODUCTION

If an element could be said to have "magical properties," it is probable that high-purity selenium would come closest to fitting this description. Despite this tribute, selenium remains a metal with an unimpressive background and an unknown and unpredictable future.

Although selenium is widely distributed in the earth's crust, the known deposits are either so small or of such low grade that they cannot be processed economically for selenium alone. Many years ago the sole source of selenium was thought to be the flue dusts from metallurgical processes utilizing sulfur ores; today, however, recovery from this source is virtually nonexistent. The anode slimes from electrolytic copper refineries are now providing the source of most of the world's selenium, and its production is centered at such refineries in the industrialized nations of the world.

The most serious problem confronting the selenium industry is its dependence on the refining of electrolytic copper, for this byproduct source is not sufficiently flexible to permit a normal supply-demand balance. The remedy, it is apparent, lies in the development of alternate sources of selenium on an economic and commercial scale. Efforts, however, to find such sources, even under a price inducement nearly double that in effect today, have not been successful.

Most of the growth in selenium output has been within the last decade. In view of the relative immaturity of this segment of the mining industry, it is not surprising that so little is known of the geology of selenium deposits and that only limited progress has been made in developing techniques in mineral beneficiation and metallurgy especially adapted to the production of this metal. Although the chemical and physical properties of selenium have been studied extensively and are fully covered in the literature, numerous problems of application to potential new uses remain unsolved.

The apparent lack of knowledge about selenium goes back to a historical attitude of aloofness. The metal had few applications at first and was looked upon as a poisonous contaminant. A program of educational promotion, with a direct appeal to those interested in both the exploitation and utilization of selenium, could eradicate much of the cautious indifference that has hampered growth in the use of this metal.

Since selenium is a strategic metal in short supply, new sources are being sought by both government and private interests. Although considerable attention has been given to this effort during the last few years, hardly any research has been published that is devoted to the recovery of the small amounts of selenium present in low-grade deposits in which the metal occurs as native selenium or as selenides of copper, silver, lead, mercury, bismuth, thallium, and iron.

In recent years, some native selenium (in both the red and gray forms) and selenides, especially iron selenide (ferroselite), reportedly have been found in the sandstones of the Morrison formation in New Mexico. •Sun and Weege (1959) encountered a sample containing considerable native selenium, in the course of working on a calibration curve for the determination of selenium by an X-ray spectroscopic method. This sample had been collected from the Marquez mine, operated by Calumet and Hecla, Inc. , near Grants, New Mexico. Similar occurrences in the same area have been reported by other writers and mine operators. Elsewhere, Wilson (1960) and the Dial Exploration Co. , of Albuquerque, New Mexico have discovered an ore body containing some selenium in the Hagan coal basin, in Sandoval County, New Mexico.

Samples from New Mexico ores submitted to the State Bureau of Mines and Mineral Resources, and assayed in the Bureau's laboratory, have contained from a trace amount to as high as 0.425 percent selenium. Some of these samples have come from uranium mines in the Grants area and represent mined ore and mill feed for uranium reduction plants. In such cases, the selenium usually is reported as an undesirable impurity and is lost in the tailings. At present, no attempt is being made to recover this waste metal.

Owing to recent advances in mining and milling technology, many valuable minor metals and mineralscan be recovered economically even though their total content in the ore may appear to be very low and unworthy of exploitation. At a price of $7 per pound for commercial-grade selenium, it would appear justifiable to investigate the possibility of recovering small amounts of

this metal contained in such ore, especially if it occurs along with other valuable metals and can be recovered as a byproduct.

In view of the economic importance of selenium and its presence in some ores from New Mexico, the metallurgical staff of the State Bureau of Mines and MineralResources undertook the present investigation on the recovery of selenium from such ores by froth flotation.

This report covers the experimental work carried out on the flotation recovery of selenium from sandstone ore samples from the Morrison formation, near Grants, New Mexico (especially Poison Canyon sandstone), and from samples of selenium ores submitted by the Dial Exploration Co. from its development work on the We Hope mining claims, in Sandoval County, New Mexico. Since many of these ores contain. uranium and molybdenum besides selenium, efforts have been made to develop procedures and flowsheets to incorporate the recovery of these associated metals as well. Realizing, moreover, the need for rapid, reliable methods for the qualitative (including field tests) and quantitative determination of selenium in ores, the Bureau has spent considerable time on developing such methods in its analytical laboratory. These methods are included in the report for the benefit of prospectors and mine -mill operator s.

Since knowledge of the economics of a metal is essential for obtaining a clear overall picture of the metal under investigation, efforts were made to include in the first part of the report a brief discussion of topics included under the broad classification of mineral economics. Selected references have been given at the end of the report for the use of those interested in obtaining more detailed information on the subject.

It is hoped that the present investigation will provide the basis for more detailed study on the recovery of selenium contained in New Mexico ores.

ECONOMICS OF SELENIUM

General

Selenium was discovered in 1817 by John Jacob Berzelius while looking for a new source of the then rare element tellurium in the flue dust from the lead chambers of the sulfuric acid plant in Gripsholm, Sweden. So closely akin were these two elements that Berzelius decided to call the former selenium, from the Greek word Selene (moon), tellurium having been derived from the Latin word tellus (the earth).

Although discovered in 1817, selenium remained but a laboratory curiosity for a little over half a century. Finally, in 1873, selenium was brought to public attention by the work of Willoughby Smith, who discovered the

particular characteristics of the electrical conductivity of selenium that helped in the development of the photoelectric cell. Thereafter, a multitude of applications developed, so that this metal now plays a definite part in everyday life.

Physical and Chemical Properties

Selenium might be described as a paradoxical element, being either a metal or a nonmetal, a conductor or a nonconductor, a colorant or a decolorant, and a hydrogenator or a dehydrogenator, as well as being either amorphous or crystalline.

The properties of selenium are understood more easily when its position in the periodic table of the elements is examined. It stands in the sixth group (VIA), between sulfur and tellurium, both of which it resembles. Like sulfur, selenium occurs in a number of allotropic forms. However, the various forms of selenium are not so well defined as those of sulfur. Selenium boils at 684. 8°C, giving off dark-red vapors; at higher temperatures it sublimes, emitting yellowish vapors. Optically, metallic selenium is pleochroic and anisotropic, having an "0" index of 3. 0 and an "E" index of 4. 04. Electrically, selenium is a photoelectric semiconductor, a property that has contributed substantially to its great value in the modern electronic world.

The chemical behavior of selenium is intermediate between that of sulfur and that of tellurium. In most respects, however, this metal can be classed with tellurium, which it more closely resembles. In all its compounds, selenium displays the properties of a nonmetal, its acid-forming tendency being especially marked in its highest valence. The valence of selenium is -2 in the hydride, +4 in the dioxide and its derivatives, and +6 in the selenates. It combines directly with hydrogen, oxygen, the halides, and sulfur, as well as with most metals.

Selenium melts at 217°C and is soluble in nitric acid (with formation of selenious acid) and concentrated sulfuric acid. It is insoluble in hydrochloric acid and is attacked only slightly by concentrated aqueous solutions of alkali hydroxides.

Geology and Mineralogy

Selenium is widely but sparsely disseminated throughout the earth's crust, averaging approximately 0. 09 ppm, and is 40th among the elements in abundance, falling between bismuth and gold.

A large area of North America, extending from Canada to Mexico and from the Mississippi River to the Rocky Mountains, is underlain by seleniferous rocks and soils. Most of the seleniferous rocks are sedimentary formations, ranging in age from the late Paleozoic era to the present. Rocks formed during the Cretaceous period have been found to be the most highly seleniferous.

Soils derived from seleniferous rocks generally contain 2 or 3 ppm selenium. Annual rainfall in the seleniferous area is not sufficient to leach even the more soluble compounds of selenium from the soil. Soils containing only 1 to 2 ppm selenium commonly sustain plants with a selenium content of 50 to 10,000 ppm. Some plants are indicative of seleniferous soils and are useful in geochemical prospecting.

Because the radii of S^{2-} (1.74 kX) and Se^{2-} (1.91 kX) are alike, selenium replaces sulfur diadochically in sulfide minerals of igneous origin. The replacement occurs more readily at elevated temperatures than at low ones. In hydrothermal rocks, in particular, selenium forms a number of selenides (silver, copper, mercury, bismuth, lead, iron, and other elements), as well as a number of complex sulfosalts, the selenium content of which may run as high as 48 percent. Some selenites are also known; e. g. , chalcomenite, Cu $[SeO_3]$ • $2H20$, and the selenites of cobalt and molybdenum, but all such minerals are rare and probably alteration products of selenides. After weathering, much of the selenium is released from these minerals and may be redeposited as ferric selenite with secondary iron minerals, such as limonite, or it may remain as native selenium.

Like sulfur, selenium is also found in nature in its native state. It occurs in both red and gray forms, and as mixed crystals, such as selentellurium (Se, Te). The oxide selenolite (SeO_2) is the oxidation product of the native element or of selenides. Selenium also accompanies sulfur in volcanic emanations. According to Goldschmidt and Hefter (1933), the S:Se ratio of sulfur sublimates of volcanic regions varies from 660:1 to 1,400:1. This ratio is similar to that in sulfides in igneous rocks. The selenium content of native sulfur of volcanic origin may be as high as 5.18 percent.

Aside from the selenium minerals themselves, magmatic sulfide deposits represent the greatest known concentration of selenium in the earth's crust. The average selenium content of such sulfides is about 0.02 percent.

There is a wide range of selenium-bearing minerals that may become of potential importance as new exploitation techniques are developed. A list of these minerals is given in Table 1.

5

TABLE 1. SELENIUM MINERALS

Native selenium - Se	Klockmannite - CuSe
Selen-tellurium - (Se,Te)	Guanajuatite - Bi_2Se_3
Selenian sulfur - (Se,S)	Penroseite - (Ni,Cu,Pb) Se_2
Aguilarite - Ag_2 (Se,S)	Wittite - Pb_5Bi_6 $(S,Se)_{14}$
Naumanite - Ag_2Se	Weibullite - $PbBi_2$ $(S,Se)_4$
Berzelianite - Cu_2Se	Platynite - $PbBi_2$ $(Se,S)_3$
Crookesite - $(Cu,Te,Ag)_2$ Se	Selenolite - SeO_2
Eucairite - CuAgSe	Ahlfeldite - Ni (SeO_4) · $6H_2O$
Umangite - Cu_3Se_2	Chalcomenite - $CuSeO_3$ · $2H_2O$
Clausthalite - PbSe	Cobaltomenite - $CoSeO_3$ · $2H_2O$
Tiemannite - HgSe	Kersterite - $PbSeO_3$ · $2H_2O$

Other minerals that occasionally contain isomorphic or interstitial selenium are native tellurium, melonite, lillianite, emmonsite, metacinnabar, and chiviatite, together with many sulfides and sulfosalts, especially those containing iron and copper.

According to Austin (1960), in the Morrison formation sandstones near Grants, New Mexico, appreciable selenium is concentrated as. ferroselite (iron selenide) and as both the red and gray forms of native selenium (mostly the gray variety). Additional studies in the Bureau's laboratory have revealed the presence of some selenium in a reddish mineral that also contains lead and molybdenum. Some selenium, moreover, has been found in massive pyrite crystals.

Production, Consumption, and Reserves

Selenium is found most frequently as an accessory mineral in base metal ores of lead, copper, and nickel, and is recoverable as a byproduct in the treatment of many of the ores of these metals. Although occurrences of selenium minerals are reported from many parts of the world, none of these are in sufficient concentration to be mined profitably for selenium alone, under present technology.

The geographic distribution of the free-world selenium industry closely follows that of the world's electrolytic copper refiners. The United States and Canada produce approximately 75 percent of the total world output.

The United States is the world's largest producer of selenium, the production having increased from 495,000 pounds in 1951 to 1,077,000 pounds in 1957. The 1958 output was 726,000 pounds, valued at about $6 million. Primary production of selenium contributes over 90 percent of the total domestic output, the remaining 10 percent coming from secondary sources.

The following six companies produce 98 percent of the present output: Allied Chemical Corp. , Marcus Hook, Pennsylvania; American Metal Climax, Inc. , Carteret, New Jersey; American Smelting & Refining Co. , Baltimore, Maryland; International Smelting & Refining Co. , Perth Amboy, New Jersey; Kawecki Chemical Co. , Boyertown, Pennsylvania; Kennecott Copper Corp. , Garfield, Utah.

Canada produced approximately 400, 000 pounds of selenium in 1958, the metal occurring in copper and copper-nickel ores in small quantities and being recovered as a byproduct. Canadian Copper Refiners, Ltd. , operates a selenium recovery plant at Montreal East, Quebec. The International Nickel Co. recovers selenium at Copper Cliff, Ontario.

The remaining free-world production is divided among a·dozen countries, although only Sweden, Japan, Belgium, West Germany, and the United Kingdom have more than a token production. The quantity of selenium produced by Russia and her satellites has not been disclosed.

Reserves of selenium are primarily a function of copper and, to a much lesser extent, lead resources. The recoverable reserve of selenium in domestic copper ores is about 25 million pounds, based on the present average recovery rate of three-fourths of a pound of selenium per ton of copper produced. It is estimated that an additional 2 to 3 million pounds of selenium is recoverable from lead ore reserves. Large tonnages of selenium are contained also in the rock strata and soils of the Western United States, and research, such as the present investigation, has been directed toward the economic recovery of the metal from the richer portions of these deposits.

Price and Tariff

The price of commercial-grade selenium increased from $1.75 a pound in 1947 to a high of $15. 50 a pound in 1956. Following the stabilization of the price in 1958, selenium of commercial grade (97. 00 to 99. 94% Se) has been selling at $7. 00 a pound, and high-purity selenium (99. 95 to 99. 99+% Se) at $9. 50 a pound. Ultra-high-purity selenium (99. 999+%) is quoted at $20 a pound. Tariff rates of 20 and 25 percent, respectively, were levied on selenium and its salts in 1909 and removed in 1913. Since that time, all selenium has remained tariff-free.

Metallurgy and Technology

Selenium can be precipitated from a solution of selenosulfates by sulfur dioxide, or from selenides by aeration of the solution. This property

is fundamental to the methods used to obtain selenium from its chief source, the "anode slimes" from copper refineries. The copper and lead ores that contribute selenium to the anode slimes also contain tellurium and other valuable impurities. As a consequence, each producer bases his extractive process on his experience, the raw material he must treat, and the product he sells.

All commercial processes may be considered as modifications or combinations of three fundamental methods: (1) smelting with soda ash; (2) roasting with soda ash; (3) roasting with sulfuric acid. In the first two methods, the selenium in the anode slimes is converted to sodium selenate, which is soluble in water. Tellurium is precipitated from the solution by neutralization with acid and recovered by filtration; then, elemental selenium is precipitated with sulfur dioxide. Selenium dioxide volatilizes and is recovered in a wet Cottrell precipitator, leaving copper and other metals behind as sulfates.

High-purity selenium is made by several methods, such as fractional distillation; zone refining; and dissolving as selenious acid, followed by purification and subsequent reduction to high-purity selenium dioxide, followed in turn by either gaseous or wet reduction.

Uses

Selenium has a wide range of applications, which are accounted for by the metal's paradoxical characteristics. One of the most important uses of selenium, although consumption of the element in this manner has been relatively small, in in the construction of light-sensitive cells. Such cells find wide application commercially in smoke detectors, burglar alarms, door openers, counters, and photographic exposure meters. In the glass industry selenium compensates for the green color of glass caused by iron oxide; in the production of red or ruby glasses, it replaces red lead and gold chloride. Although much more expensive than sulfur, selenium also has been used in recent years in the rubber industry. Among the advantages credited to selenium in rubber compounding, it is claimed that it shortens the time of cure, increases the tensile strength, improves the aging qualities, and 'increases the resistance to abrasion by as much as 50 percent. Selenium is commonly used, moreover, as a constituent of stainless steels for the purpose of increasing the speed of machining. Other applications are in the dyeing industry, in sensitizing photographic films, in fireproofing cotton or rubber, and in selenium oxychloride, which has been acclaimed as a nearly universal solvent.

Toxicity

Selenium and its compounds are referred to in the literature as highly toxic, the maximum allowable concentration in air being about 0.10 ppm.

Large quantities of selenium are handled, however, in a great variety of ways with no toxic effects upon the handlers. Contact with metallic or amorphous selenium has not been reported as a source of skin injury, although selenium salts have given rise to contact dermatitis.

Selenium, whether taken orally, inhaled as vapors, or absorbed through the skin, produces gastrointestinal disturbances and has deleterious effects upon the lungs, liver, and other organs. In acute stages of selenium "poisoning," the breath acquires a garlic odor.

Strategic Considerations

The United States, it would appear, is assured of an adequate supply of domestic selenium. A stable domestic copper industry, together with the availability of substantial quantities of selenium from Canada and Mexico, should eliminate any possibility of a serious selenium shortage under foreseeable conditions. Although a stable copper production assures selenium self-sufficiency at the current rate of consumption, this tie-in with copper precludes the rapid expansion of selenium production in the event that an unexpected increase in demand or strategic use should develop.

Selenium was placed in Group II of the Office of Civil and Defense Mobilization (OCDM) list of strategic and critical materials, issued in September 1948, In May 1953, selenium was transferred to Group I at the request of the Department of Defense, and stockpile specifications and quotas were established. In June 1956, the Defense Minerals Exploration Administration (DMEA) made selenium eligible for financial assistance in .exploration projects. This eligibility was continued when DMEA was superseded by the Office of Minerals Exploration (OME).

SELENIUM ANALYSIS

During the course of the present investigation, it was necessary to perform both the qualitative and quantitative analysis for selenium in various ore samples and metallurgical products. For this purpose, all the known analytical procedures were evaluated in order to arrive at the optimum methods of analysis. Required modifications in procedures were made where necessary.

The optimum analytical procedures established by experimentation in the Bureau's chemical laboratory were as follows:

Qualitative, Spot, and Microchemical Tests

Stannous Chloride Test

The red color of native selenium is very characteristic; when obtained, no additional test is necessary to confirm the presence of the element. The usual procedure consists of breaking down the minerals, ore and soil samples, or metallurgical products with 1:1 nitric acid and 1:5 hydrochloric acid (generally, some metallic selenium is precipitated, but most of it goes into solution , as selenious acid, H_2SeO_3), and adding a 2-percent stannous chloride solution (in 1:5 HC1) to the filtrate in order to precipitate selenium as a brick-red powder. When once precipitated, selenium cannot be taken into solutionwith nitric acid or aqua regia. Gold, mercury, and tellurium, if present in solution, will likewise be thrown down; only rarely, however, will they obscure the red color of the precipitate. This test is highly satisfactory with a lower detection limit of about 0. 025% Se.

Volatilization-Condensation Test (U. S. Bureau of Mines field test for selenium)

The U. S. Bureau of Mines has developed a simple, reliable test for field detection of selenium in rocks and soils. In this test, described by Peterson, Jensen, and Anderson (1957), two procedures are given for the qualitative detection of selenium, the choice depending upon the form of occurrence and the presence of interfering constituents in the sample. These methods involve either a pyrosulfate for a caustic fusion of the sample in a test tube to form the element selenium, which will volatilize and condense as a red deposit on the cooler, upper portion of the test tube. The methods are sensitive to 10 ppm, equivalent to 0. 001 percent, and can be made semiquantitative by using suitable standard samples.

Quantitative Analysis

Several quantitative analytical procedures for selenium are described in the technical literature, and efforts were made to evaluate these methods with respect to speed, accuracy, reliability, and simplicity. As a result, two spectrophotometric methods were developed, one for high-grade samples and the other for those of low grade.

The procedure for low-grade samples is a modification of the AmericanCyanimid Co. method for the determination of selenium in ores and cyanide solution, as described by Eiss and Giesecke (1959). The procedure for high-grade samples is a modification of the spectrophotometric determination of

selenium and tellurium in concentrated sulfuric acid described by Wiberley, Bassett, Burill, and Lyng (1953). For the given spectrophotometric methods a Bausch and Lomb "Spectronic 20" colorimeter was used. All measurements were made in 1-inch cells.

The results of the quantitative analysis obtained by the newly developed procedures were compared with the results of the analysis for selenium run by the Kawecki Chemical Co. on the same samples, and were found to check within acceptable tolerances.

Spectrophotometric <u>Determination of Selenium in Low-Grade Samples</u>

Take up to a 10-gm sample and allow it to dissolve in 1:1 HNO_3-HC I overnight at room temperature. Filter solution from the insoluble material and wash well with distilled water. Make up the solution containing selenium to a known volume and take an aliquot for assay. To prevent the loss of selenium by volatilization, arrange the sample weight and volume so that a small aliquot is used for the analysis.

Place the aliquot from the above, containing 5-35 mg of selenium, in a 100-ml beaker and evaporate gently to dryness at 75°C. Cool, add 2-5 drops of fuming HNO_3, and evaporate again just to dryness. Add 10 ml of 0. 1M EDTA [disodium salt of (ethylenedinitrilo) tetraacetic acid]. Adjust pH to 2-3 with 2.5M formic acid (about 2 ml). Add 2 ml of 0.5-percent 3.3'-diaminobenzidine hydrochloride solution (prepared fresh daily) to the solution and allow to stand for 30 minutes.

Adjust the pH to 6-7 with NH_4OH. Transfer the solution to a 125-ml reparatory funnel, add exactly 10 ml of benzene, and shake vigorously for about 30 seconds. Transfer the benzene to a 15-ml centrifuge tube and spin at 2,000 rpm for a few minutes. Separate the clear benzene layer and measure the optical density at 420 my- Run a reagent blank with each set of samples.

Prepare a calibration curve by taking 5-, 10-, 15-, 20-, 25-, and 30-mg aliquots of standard selenium and develop color as above.

<u>Spectrophotometric</u> Determination <u>of Selenium in High-Grade</u> Samples

Treat a sample of the unknown material containing from 5 to 30 mg of selenium with 1:1 HNO_3-HC1 overnight at room temperature. Filter the insoluble material from the solution and wash well with distilled water. Make the filtrate 3N with HC 1 and precipitate the selenium with 5 ml of stannous chloride solution. (The $SnCl_2$ solution is prepared by dissolving 115 gm of $SnCl_2$ in 170 ml of 12N HC 1. The resulting solution is diluted to 1 liter with distilled water and stored over tin.)

Allow the selenium precipitate to settle and then filter through a sintered-glass filter crucible (Gooch crucible). Wash precipitate with distilled water and finally with alcohol, and dry at 100°C. Add approximately 35 ml of hot concentrated H_2SO_4 to a small beaker containing the crucible and precipitate. The temperature of the acid should be 175°C and should be maintained for 15 minutes. After cooling, the solution is transferred to a 100-m1 volumetric flask and diluted to the mark with concentrated H_2SO_4. The optical density of the solution is measured at 350 mp., and the concentration obtained from the standard calibration curve.

The calibration curve is prepared by treating stock solutions containing known amounts of selenium according to the above procedure. The optical density of the sulfuric acid solution is plotted against the concentration.

RECOVERY OF SELENIUM BY FLOTATION

Theoretical Considerations

As indicated earlier in this report (p. 5), selenium occurs in nature as native selenium or as compounds of selenium, such as selenides or selenites. It is also found in appreciable amounts in magmatic sulfides and becomes available as a byproduct when these sulfide minerals are recovered for their base metal content.

For flotation considerations, the above selenium-containing minerals may be classified conveniently under three groups: (1) native selenium, (2) selenides and selenites, and (3) magmatic sulfides. Of these, the magmatic sulfides group is the only one on which considerable flotation work has been done. Each year, millions of tons of sulfide ores are treated by flotation for the recovery of base metals and the byproduct recovery of many minor metals, such as selenium. On the other hand, very little study has been devoted to the flotation characteristics of native selenium, and selenides and selenites. As a matter of fact, none of the books on flotation theory or practice mention this subject. This is understandable, for up to now selenium minerals have not been found in nature in sufficient quantities to justify flotation test work for the recovery of the metal.

It is easy for students of flotation to assume that selenium is readily floatable. The reason for this assumption is that selenium belongs to the sulfur family of elements, which it resembles closely. These elements exhibit filament crystals. In the case of selenium, the "atoms of the element are arranged in endless spirals, the interatomic distance within a spiral being 2.32 A. Adjoining spirals are parallel, and the nearest distance from an atom in one chain to an atom in the other is 3.46 A" (Gaudin, 1957, p. 33). Such filament crystals of selenium, like those of sulfur, lean toward nonpolarity, which is the prime characteristic of highly floatable minerals such as graphite and molybdenite. The label "nonpolar" refers to their indifference to water,

which is believedto be a consequence of the relative lack of ions at the mineral-water interface. Since this nonpolar property of the crystals imparts strong floatability to minerals such as graphite and molybdenite, it would not be surprising to find that refined and native selenium exhibit the same characteristic.

Furthermore, when the crystal structure of powdered refined selenium and native selenium (also in a fine-powder form), obtained from ore samples, was examined at the Institute both under a microscope at high magnifications and an electron microscope, it was revealed that the selenium crystals are acicular, often hollow and tubelike, and sometimes clustered in sheets. Such crystal structure makes selenium ideally suited for flotation. Thus, theoretically, the flotation of native selenium should be relatively simple and very effective.

In regard to the flotation characteristics of selenides and selenites, it may be assumed that because of the close resemblance of these minerals to readily floatable base metal sulfide minerals, no difficulty would be encountered in recovering these selenium-containing minerals by flotation. The general flotation treatment in the case of selenides and selenites would be simple, effective, and inexpensive. A sulfhydryl collector (e. g., potassium ethyl xanthate, Z-3), a frother (e. g., pine oil or Dow Froth), a gangue depressant (e. g., sodium silicate), and soda ash for control of pH should suffice. Soda ash is preferred to lime, as excess lime has a tendency to depress pyrites, which may contain appreciable selenium in solid solution. For the same reason, a slightly alkaline circuit is preferable to a highly alkaline one in this case.

Flotation Characteristics of Refined Selenium

The foregoing hypothetical indications of the excellent floatability of refined selenium were confirmed by actual flotation tests on commercially available selenium metal powder procured from Fisher Scientific Co. These tests were run on refined selenium powder rather than native selenium, as occurring in natural ores, because a sufficient quantity of native selenium was not available for preliminary test work. Furthermore, it is logical to assume that the behavior of commercial selenium would closely resemble that of native selenium.

In these tests small amounts of powdered selenium metal were mixed with the usual gangue minerals, including quartz, feldspars, and calcite, and such synthetic samples were subjected to flotation under general laboratory conditions. In all these tests no difficulty was encountered in floating nearly 100 percent of the selenium contained in the samples. The selenium particles were readily attachable to air bubbles, and as in the case of sulfur, graphite, and molybdenite, a frother was sufficient to recover the metal powder. More rapid flotation and a cleaner float are possible, however, if a water-insoluble hydrocarbon oil, such as kerosene, is used to smear the surface of the selenium particles.

Further test work, to determine optimum flotation conditions, resulted in the use of a reagent combination consisting of a hydrocarbon, such as kerosene, as a collector, and a soluble frother, such as Dow Froth, as a frother, in a faintly alkaline circuit obtained by the addition of soda ash and sodium silicate. Repeated cleanings were found to be advantageous.

Types of Ores Tested

The interest of the State Bureau of Mines and Mineral Resources in this project was initiated when Dr. Ming-Shan Sun, of the Bureau staff, and Mr. R. J. Weege, of Calumet and Hecla, Inc. , reported the occurrence of appreciable amounts of native selenium in the sample collected from the Marquez mine, operated by the Uranium Division of Calumet and Hecla, Inc. , in section 23, T. 13 N. , R. 9 W. , McKinley County, New Mexico, about 20 miles north of Grants.

Most of the flotation test work was carried out on sandstone ore samples collected from uranium properties located in the Grants area. In these deposits, the selenium is concentrated in the so-called Poison Canyon sandstone, which occupies the middle part of the Brushy Basin member of the Jurassic Morrison formation. This sandstone is the major uranium-bearing sediment in the vicinity of Poison Canyon and in the general Ambrosia Lake area.

The selenium content in these ore samples ranged from as high as 0.435 percent to as low as 0. 021 percent.

After the inauguration of this project in March 1960, a few samples from the Dial Exploration Co., Inc., Albuquerque, New Mexico, were received by the Bureau for evaluation of their selenium content. These samples of selenium-bearing shaly sandstones and sandy shales came from the Company's uranium claims located in the Hagan coal basin in Sandoval County, New Mexico. This area is approximately midway between Albuquerque and Santa Fe, New Mexico. Stratigraphically, the claims lie on the Mesozoic-Cenozoic boundary, the most heavily mineralized areas occurring in the two upper, bleached zones of the Galisteo formation, of Tertiary age. Uranium mineralization in this area is accompanied by some selenium. Outcrops of the mineralized horizons are covered with a heavy growth of selenium indicator plants, such as Astragalus and Stanleya.

The samples obtained from the Dial Co. 's deposit contained about 0. 03 percent selenium, most of which was identified as native selenium. The uranium content of these samples was so low that they were not considered a uranium ore.

For convenience' sake, in reporting the experimental test work, the types of ores treated will be classified under two categories: (a) sandstone

ores from the Morrison formation, from the Grants area, especially from the vicinity of Poison Canyon and Ambrosia Lake; and (b) sandstone ores from the Galisteo formation, from the Dial Exploration Co. 's claims located in the Hagan coal basin, in Sandoval County.

Sample Preparation

The run-of-the-mine samples as received by the laboratory were stage crushed through a jaw crusher, and then through crushing rolls, to obtain a minus-10-mesh product. A few large pieces from the uncrushed samples were set aside for petrographic and mineralogic studies. The crushed product was thoroughly mixed, and 600-gram samples for test work were obtained with the aid of a Jones splitter. A head sample for selenium analysis also was obtained from each ore sample, and analyzed for its selenium content.

EXPERIMENTAL PROCEDURES AND RESULTS

Sandstone Ores From Morrison Formation

Preliminary Test Work on Sandstone Ore No. 1

In order to obtain the required information on the association of selenium in the ores and to establish the economic limit for liberating and grinding, preliminary tests were carried out on samples of sandstone ore No. 1 from the Morrison formation. The ore sample contained 0.436 percent selenium and was selected for preliminary testing because of its high selenium content; the ore was similar to the rest of the sandstone ores from the Morrison formation and was considered representative of such ores. The testing included size-assay analysis, microscopic examination, and tests for determination of the optimum grind.

Size-Assay Analysis and Microscopic Examination

The size-assay analysis for the ore sample under investigation was as follows:

TABLE 2. SIZE-ASSAY ANALYSIS OF SANDSTONE ORE NO. 1

Size, mesh	Weight (%)	Assay (% Se)	Distribution (% Se)
Minus-10, plus-28	22.8	.734	33.5
Minus-28, plus-48	14.5	.438	14.7
Minus-48, plus-100	52.0	.193	22.9
Minus-100, plus-200	7.3	.364	6.2
Minus-200	3.4	2.26	17.7
Composite, head sample	100.0	.436	100.0

The size fractions covered by the above analysis were examined under the microscope in order to study the association of the selenium minerals with the gangue, and to obtain necessary information regarding liberation behavior and the fineness of grind required.

The size-assay analysis and the microscopic examination revealed that about 20 precept of the total selenium content was distributed in the finer sizes (below 200 mesh) of the screened products in the form of black powdery material. Another 30 percent of the total selenium was tied up in the intermediate sizes (minus-48, plus-200 mesh) either in selenite grains or in massive pyrite crystals. The remaining 50 percent was contained in the coarse sizes above 48-mesh as inclusions of native selenium and selenides in coarse agglomerates of sand grains.

Such an occurrence of selenium suggested careful grinding of the samples for disintegration of the sandstone in order to free the individual sand grains, yet without subdividing the grains themselves. Moreover, it would be desirable to have some sort of scrubbing action during grinding, to knock off the crusts of native selenium adhering to the sand grains.

The results of the above size-assay analysis and of the microscopic examination indicated that a 48-mesh grind is sufficient to achieve the required degree of liberation of selenium from this ore sample, as well as from similar sandstone ores from the same area. Furthermore, in order to obtain the optimum grind, it would be advantageous to utilize a rod-mill grind rather than a ball-mill grind, the latter having a tendency to produce excessive slimes.

Optimum Grinding Procedure

All samples were ground in an 8-inch-diameter x 11-inch laboratory rod mill operating at 60 rpm and containing 9. 8 kilograms of cold-rolled steel rods ranging in diameter from 1-1/4 inches to one-fourth inch. Grinding tests were run on 600-gram samples of minus-10-mesh product at 66 percent solids. Socorro tapwater, having a pH of 7.2-7.3 was used in all the grinding tests.

The results of the grinding tests on sandstone ore No. 1 indicated that the grinding time required for obtaining the desired 48-mesh grind was 6 minutes. A typical screen analysis of the ground ore was as follows:

TABLE 3. SCREEN ANALYSIS OF GROUND SAMPLE OF SANDSTONE ORE NO. 1

Size, mesh	Weight (%)	Cumulative weight (%)
Plus-48	2.5	2.5
Minus-48, plus-65	36.8	39.3
Minus-65, plus-100	35.9	75.2
Minus-100, plus-150	11.0	86.2
Minus-150, plus-200	6.7	92.9
Minus-200, plus-325	3.4	96.3
Minus-325	3.7	100.0
	100.0	

The above screen analysis indicated that an excellent grind was obtained by grinding in the rod mill for 6 minutes. About 75 percent of the total weight was above 100 mesh, and more than 92 percent of the weight was above 200 mesh. Moreover, the amount of slimes (minus-200 mesh) was kept at a minimum, amounting to only 7 percent of the total weight.

Flotation Test Work on Sandstone Ore No. 1

All the flotation tests were run in the 600-gram Fagergren (Wemco) laboratory flotation machine, having an impeller speed of 1,750 rpm, on ground pulps containing about 25 percent solids. Socorro tapwater, having 7.2-7.3 pH, was used throughout the testing, and the temperature of the pulp was normally between 22⁰ and 25°C. The reagents used were all commercially available products; they included various xanthates, kerosene, pine oil, Dow Froth 250, soda ash, and sodium silicate. Xanthates were added to the pulp in a 1-percent solution, and because of the alteration that occurs in xanthate solutions with time, fresh solutions were made daily. Kerosene, pine oil, and Dow Froth 250 were added without dilution; whereas soda ash and sodium silicate were added in 5-percent solutions.

Great care was taken throughout the flotation testing to keep all the standard conditions constant and to observe all the necessary requirements during preparation of the charge, grinding, weighing, measuring, sample preparation for analysis, and so on.

Since the aim of the investigation was to devise a practical flowsheet for selenium flotation from natural ores, efforts were made to conduct the test work so that it would simulate the actual conditions met in practice, and which might easily be duplicated in the field.

Determination of Optimum Flotation Conditions

Before establishing a standard selenium flotation test procedure and flowsheet, various preliminary flotation tests were carried out on sandstone ore No. 1 to determine the optimum flotation conditions; namely, the appropriate collectors, auxiliary promoters, frothers, conditioning agents, and gangue depressants, as well as their optimum amounts; conditioning and flotation time; pH; temperature of the pulp; percent solids during flotation; and cleaning of the rougher concentrates.

The typical flotation test in this phase of the investigation consisted of conditioning the properly ground ore in the laboratory flotation cell at 25 percent solids for 3 minutes with the desired amounts of conditioning agents, collector, and frother, and subjecting the conditioned pulp to flotation for 5 minutes. Necessary modifications in the above test procedure were made whenever necessary in order to achieve the optimum with respect to collection, froth conditions, grade of concentrates, and recovery of selenium.

Several series of flotation tests were conducted under identical conditions except for the variable (or condition under investigation), which was varied from test to test in each series in order to establish the optimum.

The results of the above series of tests are summarized below.

Conditioning Agents

For optimum flotation conditions, it is usually necessary to condition the pulp prior to the addition of the collector, to insure the desired collection on the surface of the specific minerals that are to be floated. Since the sandstone ores under investigation had been partially altered as the result of natural oxidizing conditions, the ground pulp was slightly acidic. It was necessary to add soda ash in the rod-mill grinding stage to overcome the acidity and neutralize the soluble salts .that would be detrimental to subsequent flotation procedure. One pound of soda ash per ton was found sufficient for this purpose.

In order to assure, moreover, a selective selenium concentrate, it was necessary to add sodium silicate as a depressant for the gangue minerals and their slimes. The, optimum amount of sodium silicate established by experimentation was 1. 5 pounds per ton of ore treated. The use of soda ash and sodium silicate in the optimum amounts resulted in a pulp having a pH of 8. 5.

Appropriate Collector and Auxiliary Promoter

The theoretical considerations for selenium flotation and the results of the flotation of refined selenium powder had indicated that a neutral oil, such as kerosene, was sufficient to float native and refined selenium. }lowever, anionic sulphydryl collectors, such as xanthates, thiophosphates or mercaptans, were found necessary for floating selenides and selenium-containing pyrites. Since the ores under investigation contained both the native and the combined forms of selenium, various neutral oils and sulphydryl collectors were tested systematically in order to determine the best collectors.

The neutral oils investigated were a neutral crude oil, No. 1 and No. 2 fuel oils, SAE No. 20 lubricating oil, and kerosene. These oils were added dropwise to the pulp in quantities ranging from 0.05 to 0. 5 pound per ton of feed.

All the neutral oils were found to be effective collectors for native selenium and some sulfides. The more viscous oils required, however, a longer conditioning period for optimum collection. For obvious reasons, kerosene at 0.1 pound per ton was selected as the optimum collector. In practice, it would be preferable to select the cheapest available neutral oil that would give the desirable results.

In regard to the sulphydryl collectors, comparative tests were run using xanthates, mercaptans, and thiophosphates. All these were found to be excellent collectors for the selenides and pyrites. Xanthates were selected, however, because of economy and availability.

Several series of flotation tests were conducted to determine the most effective xanthate. Ethyl (Z-3 and Z-4), isopropyl (Z-9 and Z-11), butyl (Z-8 and Z-12), amyl (Z-5 and Z-6), and hexyl (Z-10) homologs in quantities of from 0. 04 to 0. 06 pound per ton of feed were tested.

Table 4 gives the results of these tests, from which it is apparent that although all the homologs were excellent collectors for native selenium, selenides, and pyrites, potassium amyl xanthate (Z-6) gave the best collection and froth condition. The lower xanthates, ethyl, isopropyl, and butyl, gave cleaner but tighter froth, which was difficult to remove even with the assistance of the frother. On the other hand, hexyl xanthate (Z-10) gave a voluminous froth of lower grade. In practice, the combination of a lower xanthate, such as ethyl (Z-3), and a higher xanthate, such as amyl (Z-6), may provide the most desirable collection as well as froth condition.

From the results of the test work in regard to the selection of the optimum collector and auxiliary promoter, the following combination was found to be the most effective:

Collector	Amount
Kerosene	0. 10 lb/ton
Potassium Amyl Xanthate (Z-6)	0. 05 lb/ton

TABLE 4. RESULTS OF FLOTATION TESTS WITH VARIOUS XANTHATES

Xanthate used	Concentrate grade (% Se)	Distribution (% Se)	Quality of flotation
Ethyl (potassium), Z-3	4.93	87.6	Cleanest, but tight froth
Ethyl (sodium), Z-4	4.86	87.8	Cleanest, but tight froth
Isopropyl (potassium), Z-9	4.73	88.2	Very clean, but tight froth
Isopropyl (sodium), Z-11	4.53	88.7	Very clean, but tight froth
Secondary butyl (potassium), Z-8	4.32	90.5	Very clean, and less tight froth
Secondary butyl (sodium), Z-12	4.30	90.1	Very clean, and less tight froth
Secondary amyl (potassium), Z-5	4.28	92.3	Clean, and desirable froth
Amyl (potassium), Z-6	4.26	92.4	Clean, and desirable froth
Hexyl (potassium), Z-10	3.72	92.8	Dirty, and voluminous froth

Appropriate Frother

Three types of commercially available frothers were investigated to create the desirable froth in combination with the optimum amounts of collectors. Pine oil, Dow Froth 250 (alcohol type), and Methylisobutylcarbinol (a higher alcohol-type frother)were tested under identical conditions. The amount of frother used was 0.1 pound per ton of feed.

Table 5 presents the results of these tests, from which it is clear that pine oil, owing to its lack of selectivity, is not desirable. On the other hand, both Dow Froth 250 and Methylisobutylcarbinol are excellent frothers, and the relative cost would govern the selection of one of them in practice. In the present investigation, Dow Froth 250 was selected for the standard test procedure.

TABLE 5. RESULTS OF FLOTATION TESTS WITH VARIOUS FROTHERS

Frother used	Concentrate grade (% Se)	Distribution (% Se)	Quality of froth
Pine oil	3.35	92.8	Voluminous and dirty
Dow Froth 250	4.30	94.8	Controllable and cleaner
Methylisobutylcarbinol	4.28	94.6	Controllable and cleaner

Time of Conditioning and Flotation

A series of tests were run in order to determine the optimum time of conditioning and flotation. In flotation procedures employing xanthates, the time of conditioning is usually very short, a matter of 1 or 2 minutes. When, however, a neutral oil, such as kerosene, is used as a collector, a longer period of conditioning is required, owing to the slower emulsification rate of oil in water.

In the present investigation, it was determined that at least 3 minutes of conditioning time was necessary in the laboratory flotation machine to obtain good results. This time can be reduced to 1 minute by adding the collectors in the rod mill during grinding. This technique could be used in actual plant practice to obtain additional conditioning time and immediate collection on the valuable particles as soon as they are liberated.

In regard to the flotation time, it was observed that although substantial amounts of selenium were floated during the first 3 minutes, it took a total of 5 minutes to obtain optimum recoveries. This additional time was attributed to the slow-floating character of the very fine particles (below 20 microns) of native selenium.

Optimum pH

As stated previously, the use of soda ash and sodium silicate as required conditioning agents brought the pH of the pulp to 8. 5. At this pH, the flotation conditions were satisfactory, and the flotation test results excellent. Further efforts to determine the effect of pH on flotation conditions and results indicated that a pH range from 7. 2 to 10. 0 was a workable range, within which

neither the flotation conditions nor the results were affected. However, above 10. 0 pH (which had to be regulated with the use of lime), the recovery of selenium decreased with higher pH. This detrimental effect of higher pH on flotation was as expected, because the use of excess lime invariably results in the depression of pyrites. Since the pyrites in the Morrison sandstone contain some selenium, their depression in flotation results in the loss of selenium and, therefore, in a decrease in recovery.

Flotation conditions and results were also adversely affected by lowering the pH below 7. 2. Although at lower pH pyritic material showed activation, the flotation of native selenium was poor. Furthermore, at lower pH xanthates decomposed, giving very poor collection and thus lower recoveries.

Effect of Temperature on Flotation

The results of the tests carried out to determine the effect of temperature of the pulp on flotation indicate that under normal plant conditions, the temperature of the pulp is not a critical factor affecting the flotation conditions or results. A temperature range from 10°C to 94°C (50°F to 201°F) was investigated, and no difficulty in flotation was encountered up to 55°C (130°F). Above this temperature, flotation conditions and results were adversely affected, most probably owing to the decomposition of xanthate, as well as neutral oil, at higher temperatures.

In actual plant practice, the temperature of the pulp would be considerably lower than the critical temperature of 55°C. On the other hand, a little longer time of conditioning may be required with lower temperature pulps during the winter months, to obtain sufficient emulsification of neutral oils in cold water. However, addition of collectors during the grinding stage may overcome this difficulty.

Percentage of Solids in Flotation Pulp

All the flotation tests up to this stage had been run at 25 percent solids in the pulp. In plant practice, however, it would be advantageous, from the point of view of both economics and efficiency, to carry out flotation at higher percent solids. This would be especially true if the tailings from the selenium recovery circuit were to be treated further for the recovery of other metals, such as uranium and molybdenum, from the same ore. In this case it would be desirable to carry out flotation at as high a percent solids as possible (for instance, as high as 50 percent solids), so that the tailings after the flotation of selenium could be taken directly to the uranium-leaching stage, thereby bypassing the thickening step in the process.

Therefore, in the next series of tests, efforts were made to determine the effect on flotation conditions and results of increasing percent solids in the pulp. Comparative tests were run at 25, 30, 35, 40, 45, and 50 percent solids.

Table 6 shows the results of these tests, which indicate that it is possible to carry out flotation at higher percent solids (up to 40 percent) without adverse effect on flotation conditions or results. On the contrary, flotation conditions and the grade of selenium concentrate were improved at higher percent solids up to the optimum limit. This was probably due to the presence of a larger quantity of highly floatable valuable particles per unit volume, these • particles having the tendency to displace the trapped gangue minerals in the froth.

For pulps containing more than 40 percent solids, although the flotation conditions were good, the recoveries began to drop. This adverse effect was due to the presence of a larger quantity of slower floating, finer sizes of selenium minerals, which were not removed from the pulp in the specified flotation time of 5 minutes.

The above hypothesis was confirmed by prolonging the time of flotation from 5 minutes to 6. 5 minutes in the case of 45 percent solids, and to 8 minutes in the case of 50 percent solids. In both these cases, by extending the time of flotation, the recoveries of selenium were increased to the original level.

TABLE 6. EFFECT OF PERCENT SOLIDS IN FLOTATION PULP

Percent solids	Concentrate grade (% Se)	Distribution (% Se)	Flotation conditions
20	4.23	94.3	Fair, light loaded
25	4.28	94.6	Good, well loaded
30	4.29	94.8	Better, well loaded
35	4.31	94.9	Best, well loaded
40	4.42	94.7	Good, heavily loaded
45	4.22	92.2	Fair, light loaded
50	3.96	89.7	Poor, slow flotation

Cleaner Flotation

Cleaning in froth flotation is effected by refloating rough or primary concentrate, usually in a much more dilute pulp than that present in the rougher circuit. The main reason for cleaning the rough concentrate is to bring the grade of the concentrate up to the level required for marketability. In the case of selenium concentrates, the buyers usually will accept a selenium product

containing more than 4 percent selenium, inasmuch as most of the anode slimes from copper refineries contain from 4 to 25 percent selenium. Moreover, the higher the grade of the concentrate, the lower are the freight rates and smelter penalties.

In flotation processes, the grade of the rougher concentrate usually is governed' by the amount of valuable metal contained in the flotation feed. Thus, for feeds containing about 0.4 percent selenium, it was possible to obtain rougher concentrate assaying from 7 to 10 percent selenium. On the other hand, for feeds containing about 0.03 percent selenium, it was possible to obtain only rougher concentrate assaying less than 3 percent selenium.

Since the primary aim in the rougher flotation is to obtain maximum recoveries of the valuable metal, the grade is usually sacrificed at the expense of recovery. In the cleaner flotation, however, the primary aim is to obtain the highest grade economically possible. In usual flotation practice, one, two, or more cleaner flotation stages may be required to obtain the desired grade. In all these cleaner stages, the cleaner tails are recirculated at the head of the previous cleaner stage or the rougher stage. A 2. 5-minute cleaner flotation time was sufficient to obtain optimum grades.

In the present investigation, efforts were made to clean the rougher concentrate at least once. No further additions of reagents were made in the cleaner flotation stage except for a little frother to obtain desirable froth.

The results of the cleaner flotation tests indicated that it was possible to obtain a concentrate having better than 4 percent selenium for low-grade ores, and as high as 52 percent selenium for higher grade ores.

Standard Flotation Test Procedure

From the results of the test work carried out in order to establish optimum flotation conditions, the following standard flotation test procedure was developed:

Sample
600 grams of minus-10-mesh ore.

Procedure
1. The sample was ground to approximately minus-48-mesh size in the laboratory rod mill for 6 minutes with 1.0 pound of soda ash and 1.5 pounds of sodium silicate per ton of ore.
2. The ground pulp was transferred to the laboratory Fagergren flotation cell, and Socorro tapwater was added to obtain about 35 percent solids in the pulp.

24

3. One-tenth pound of kerosene, 0. 05 pound of potassium amyl xanthate (Z-6), and 0.1 pound of Dow Froth 250 per ton of ore were added to the pulp and conditioned for 3 minutes. The pH of the pulp was about 8. 5.
4. The conditioned pulp was subjected to flotation for 5 minutes. The pH of the tailing was 8.4.
5. Cleaner flotation: In the case of cleaner flotation, the rougher concentrate was refloated in the flotation machine, without additional reagents, to obtain the cleaner concentrate.

Results of Flotation Tests on Sandstone Ores

The sandstone ore samples from the general vicinity of the Grants area were subjected to flotation according to the above standard test procedure, in order to evaluate the amenability of these selenium-containing 'ores to the flotation procedure.

Five tests were run on each ore sample under identical conditions. **The** average of the results of these five tests was taken as representative of the ore sample in question. The samples contained selenium in concentrations as high as 0.435 percent and as low as 0. 021 percent.

Table **7** shows the average results of the ore samples investigated. From these results it is apparent that good recoveries in the rougher circuit ranging from 82 to 97 percent, and acceptable grades of selenium cleaner concentrates ranging from 3 to 16 percent, are obtained by treating the ores with a simple flotation procedure. It is also apparent that both high-grade and low-grade ores respond to the flotation technique. The flotation results are di.. rectly proportional, of course, to the amount of selenium contained in the feed. Feeds containing higher concentrations of selenium offer better results, as regards both recovery and grade.

Sandstone Ores From the Galisteo Formation (Dial Ores)

Preliminary Test Work on Dial Ore No. 1

In order to obtain information on the association of selenium in the sandstone ores from the Galisteo formation and to establish the economic limit for liberation and grinding, preliminary tests were carried out on samples of Dial ore No. 1 containing 0. 031 percent selenium.

TABLE 7. RESULTS OF FLOTATION TESTS ON SANDSTONE ORES FROM MORRISON FORMATION

Ores tested	Heads	Cleaner concentrate		Cleaner tailing		Rougher concentrates (calculated)		Rougher tailing		Distribution (% Se)	
	(% Se)	(% Wt)	(% Se)	(% Wt)	(% Se)	(% Wt)	(% Se)	(% Wt)	(% Se)	Cleaner	Rougher
Sandstone Ore No. 1	0.432	2.50	16.32	3.32	0.452	5.82	7.27	94.18	0.013	93.60	97.06
Sandstone Ore No. 2	0.344	2.30	13.86	4.60	0.392	6.90	4.86	93.10	0.008	92.54	97.74
Sandstone Ore No. 3	0.109	1.63	5.54	4.64	0.273	6.27	1.63	93.73	0.007	82.34	94.00
Sandstone Ore No. 4	0.030	0.63	3.72	2.79	0.062	3.42	0.735	96.58	0.005	78.20	83.96
Sandstone Ore No. 5	0.028	0.62	3.22	3.55	0.092	4.17	0.555	95.83	0.005	71.30	82.95
Sandstone Ore No. 6	0.079	1.37	5.17	5.82	0.062	7.19	1.040	92.81	0.005	88.40	92.96
Sandstone Ore No. 7	0.027	0.68	3.03	4.84	.054	5.52	0.421	94.48	0.004	76.30	86.00
Sandstone Ore No. 8	0.021	0.58	2.86	3.42	.034	4.04	0.425	95.96	0.004	76.10	81.62

Size-Assay Analysis and Microscopic Examination

The size-assay analysis of Dial Ore No. 1 crushed through 10-mesh screen was as follows:

TABLE 8. SIZE-ASSAY ANALYSIS OF DIAL ORE NO. 1

Size, mesh	Weight (%)	Assay (% Se)	Distribution (% Se)
Minus-10, plus-28	65.8	.022	45.20
Minus-28, plus-48	11.6	.020	7.25
Minus-48, plus-100	7.9	.019	4.69
Minus-100, plus-200	5.1	.025	4.00
Minus-200	9.6	.129	38.86
Composite, head sample	100.0	.031	100.00

The size-assay analysis and the microscopic examination of particles in the above mesh size revealed that about 39 percent of the total selenium was contained in the finer sizes below 200-mesh, occurring in the form of black slimy material, which was identified as native selenium by X-ray analysis. About 9 percent of the selenium was tied up in the intermediate minus-20 to plus-200-mesh size. In this case, however, the selenium appeared to be in the form of coatings of native selenium on coarse gangue particles, which immediately suggested the necessity of some sort of scrubbing action during grinding. The remaining 52 percent of selenium was contained in the coarser fractions above 48-mesh, occurring probably as native selenium in coarse shaly material or in the sandstone agglomerates.

The above preliminary examination indicated that a 48-mesh grind accompanied by scrubbing action would be sufficient to liberate the selenium in this ore. Furthermore, it was noted that most of the coarse particles had a tendency to disintegrate when pressed between the fingers, owing to the presence of a considerable amount of soft altered material, mostly limonitic. For this reason, difficulties in grinding and flotation were to be expected.

In view of the above findings, it was felt that in the case of the Dial ores it would be necessary to grind the samples very carefully so as not to produce excessive slimes, and yet at the same time obtain a 48-mesh grind in order to liberate the selenium tied up in plus-48-mesh material.

On further examination of the Dial ore samples, it was determined that mere soaking in water helped to disintegrate the coarser particles and

liberate the particles of selenium. This disintegration was enhanced further by agitation of the samples in the laboratory Fagergren flotation machine for a few minutes.

The size-assay analysis of the product resulting from a 5-minute agitation of Dial ore No. 1 in the laboratory Fagergren machine was as follows:

TABLE 9. SIZE-ASSAY ANALYSIS OF DIAL ORE NO. 1 AFTER AGITATION

Size, mesh	Weight (%)	Assay (% Se)	Distribution (% Se)
Plus-48	8.6	0.040	10.40
Minus-48, plus-65	3.1	.017	1.60
Minus-65, plus-100	4.2	.004	0.51
Minus-100, plus-150	5.6	.005	0.86
Minus-150, plus-200	3.8	.006	0.69
Minus-200, plus-325	10.1	.013	3.94
Minus-325	64.6	.042	82.00
Composite, head sample	100.0	.031	100.00

The above results indicated that agitation in the flotation machine was sufficient to disintegrate the coarse agglomerates, except for about 10 percent of the sample, which constituted hard shaly material and was unaffected by agitation. Since this harder fraction was found to contain about 12 percent of the total selenium content, it was deemed necessary to grind this fraction through 48-mesh screen in order to liberate the contained selenium.

In this case also, it was thought advisable to utilize a rod-mill grind, which not only would avoid overgrinding but would provide the desired scrubbing action. The grinding procedure would then consist of subdividing only the hard, coarser fraction remaining after the removal of the fine sizes produced by suitable agitation.

Optimum Grinding Procedure

For the Dial ore samples, the following grinding procedure was found to give a suitable product for flotation:
1. A 600-gram sample was agitated in the laboratory Fagergren flotation machine for 5 minutes, at 50 percent solids.

28

2. The agitated pulp was next screened through a 48-mesh sieve.
3. The plus-48-mesh product was then ground in the laboratory rod mill (the same rod mill and the same conditions as in the case of previous ores) for 3 minutes, at 66 percent solids.
4. The ground ore was combined with the minus-48-mesh screened product.

Flotation Test Work on Dial Ore No. 1

The test conditions and general flotation procedure followed for the Dial ore samples from the Galisteo formation were the same as those employed for the sandstone ores from the Morrison formation.

In the preliminary flotation testing, efforts were made to determine the optimum conditions with regard to collectors, auxiliary promoter, frother, conditioning agent, pH, time of conditioning and flotation, and cleaner flotation requirements. As expected, the results of such testing were very close to those obtained in the case of the previous ores, except for the conditioning step, which was found to be the most important phase in the flotation removal of selenium from the Dial ore.

It was pointed out previously (p. 27) that the Dial ore had a tendency to disintegrate and slime badly when pressed between the fingers or when subjected to mere soaking and agitation in the laboratory flotation machine. An examination of the size-assay analysis shown in Table 9 reveals that after a 5-minute agitation in the Fagergren machine, about 65 percent, by weight, of the total sample passed through a 325-mesh screen. Since this slime fraction contained most of the altered products, such as clays and limonite, along with a small amount of liberated selenium, it was not surprising to encounter difficulties in flotation due to the presence of this detrimental fraction.

During the preliminary test work, the typical obstructions to flotation characteristic of slimes, such as consumption of reagent, overfrothing, contamination of concentrate, and reduction in recovery, were experienced. These difficulties, however, were partially overcome by the addition of a larger amount of sodium silicate, a strong slime depressant, and were more substantially eliminated by longer conditioning with the depressant. Continued experimentation revealed that the optimum amount of sodium silicate and the most favorable period of conditioning were 2.5 pounds per ton and 15 minutes respectively.

Standard Flotation Test Procedure

From the results of the preliminary testing for the determination of optimum conditions, the following standard flotation test procedure was developed.

Sample
600 grams of minus-10-mesh ore.

Procedure
1. The sample was agitated in the laboratory Fagergren flotation machine, at 50 percent solids, for 5 minutes.
2. The pulp was screened through a 48-mesh screen.
3. The plus-48-mesh product was ground in the laboratory rod mill for 3 minutes, at 66 percent solids, to obtain a 48-mesh grind.
4. The ground material was mixed with the minus-48-mesh screened product, the pulp was transferred to the flotation machine, and tapwater was added to obtain about 35 percent solids.
5. The pulp was conditioned for 15 minutes with 1.0 pound of sodium carbonate and 2.5 pounds of sodium silicate per ton of ore treated. The pH of the pulp was 8.8.
6. After thorough conditioning with a slime depressant, the pulp was further conditioned for 3 minutes with 0.1 pound of kerosene, 0.05 pound of potassium amyl xanthate (Z-6), and 0.1 pound of Dow Froth 250 per ton of ore treated.
7. The pulp was subjected to flotation for 5 minutes. The pH of the tailings was 8.7.
8. Cleaner flotation: The rougher selenium concentrate was cleaned once by refloating in the flotation machine without additional reagents.

Results of Flotation Tests on Dial Ores

Two different Dial ore samples were subjected to flotation according to the above standard test procedure, in order to evaluate the amenability of these selenium-containing ores to the flotation procedure.

In the first two series of flotation tests, five tests were run on each of two ore samples under identical conditions. The average of the results of these five tests was taken as representative of the ore sample in question. The selenium content in these ores was about 0. 03 percent.

While running the tests in the first two series, it was observed that because of the very small weight of selenium (about 0.2 gram of selenium in a 600-gram ore sample) in the flotation feed, the rougher selenium concentrate did not contain enough selenium to. provide a desirable load in the cleaner step.

TABLE 10. RESULTS OF FLOTATION TESTS ON SANDSTONE ORES FROM GALISTEO FORMATION
(DIAL ORES)

Test series number	Dial ore number	Heads	Cleaner concentrate		Cleaner tailing		Rougher concentrate (calculated)		Rougher tailing		Distribution (% Se)	
		(% Se)	(% Wt)	(% Se)	(% Wt)	(% Se)	(% Wt)	(% Se)	(% Wt)	(% Se)	Cleaner	Rougher
1	1	.031	0.92	2.20	5.12	0.152	6.04	0.465	93.96	0.004	63.60	88.12
2	2	.032	1.04	1.94	5.32	0.144	6.36	0.436	93.64	0.005	62.00	85.58
3	1	.031	0.58	4.04	5.62	0.061	6.20	0.432	93.80	0.005	74.35	85.07
4	2	.032	0.61	4.12	5.59	0.058	6.20	0.461	93.80	0.005	77.59	88.30

31

This difficulty resulted in a cleaner concentrate of lower grade and increased losses in the cleaner tail.

For this reason, in the next two series of flotation tests, efforts were made to obtain larger amounts of rougher concentrates for the cleaning step by combining the products resulting from the five separate tests conducted under identical conditions on each ore sample. In this way, a rougher concentrate that contained sufficient selenium mineral load for the cleaner flotation step was obtained. This combined rougher concentrate was then cleaned once to obtain a cleaner concentrate and a cleaner tail. The rougher tailings from these five tests were combined to obtain a total rougher tail.

Table 10 shows the results of the four series of tests run on the Dial ores. From these results it is evident that recoveries of better than 85 percent and grades of cleaner concentrates ranging from 2 to 4 percent can be obtained by the flotation treatment of Dial ores. The grades of cleaner concentrates in test series 1 and 2 are somewhat low, owing to the lower content of selenium in the feed. By increasing the load in the cleaner step it was possible, however, to obtain acceptable grades above 4 percent, as indicated by the results of test series 3 and 4.
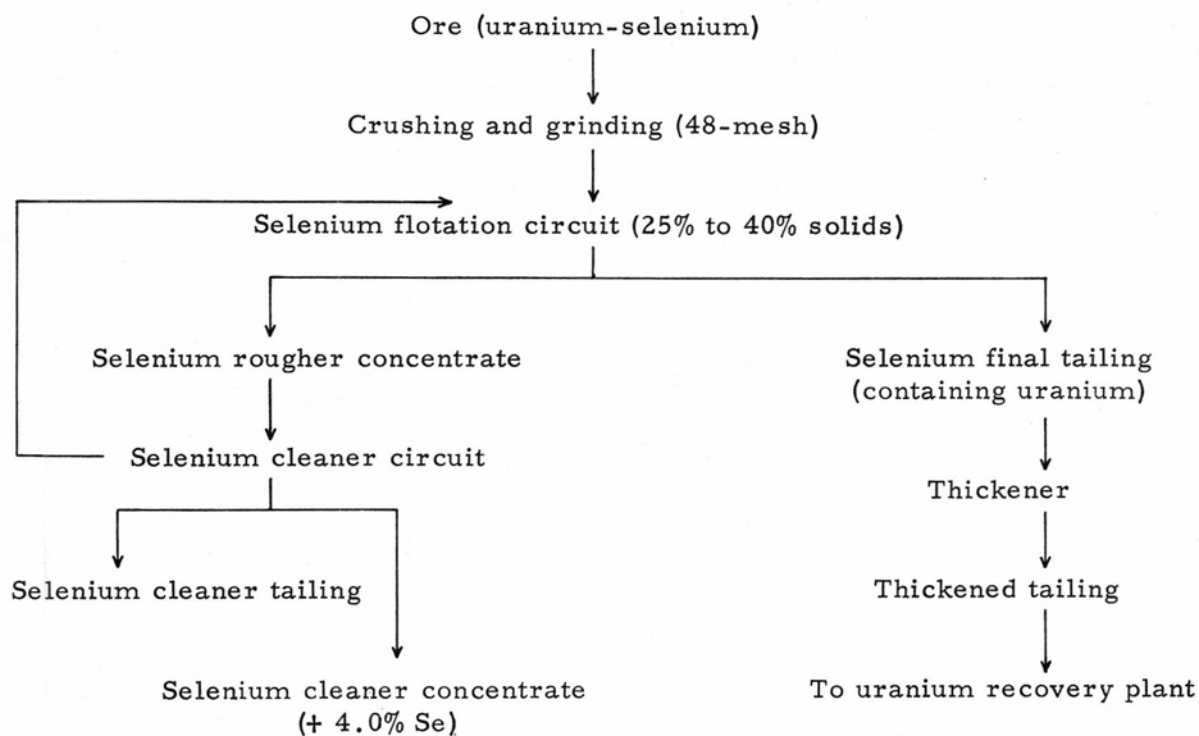

TREATMENT OF COMPLEX ORES

In natural ores, many other metals besides selenium often are found to be present. In such cases, selenium is usually a minor constituent and can be recovered as a byproduct. For example, the sandstone ores from the Morrison formation are exploited primarily for their uranium content, because uranium is the major constituent in these ores, whereas vanadium, molybdenum, and selenium are present in only minor amounts. At present, vanadium is the only minor metal recovered as a byproduct from these uranium ores. It is possible, however, to recover selenium, as well as molybdenum, with improved technology and under favorable economic conditions.

In complex ores containing more than one valuable metal, it is imperative that the recovery of byproduct metals should not impede in any way the maximum recovery of the major metal. Conversely, every effort should be made to recover the byproduct metals where such recovery is economically justified.

Since the results of the present investigation have shown that selenium, whether as native selenium or as sulfides, can be recovered readily by flotation under appropriate conditions, it is logical, in the case of complex ores, first to remove the selenium by flotation, and then to treat the tailings from the selenium circuit for the extraction of other metals.

Uranium-Selenium Ores

As pointed out above, in the case of uranium-selenium ores, the selenium should be removed by flotation prior to the extraction of uranium. For such ores, as represented by those from the Morrison sandstone in Poison Canyon and other similar ores, the following treatment procedure and flowsheet should give the optimum recovery of both these metals.

Ore (uranium-selenium)
↓
Crushing and grinding (48-mesh)
↓
Selenium flotation circuit (25% to 40% solids)

Selenium rougher concentrate

Selenium final tailing
(containing uranium)
↓
Thickener
↓
Thickened tailing
↓
To uranium recovery plant

Selenium cleaner circuit

Selenium cleaner tailing

Selenium cleaner concentrate
(+ 4.0% Se)
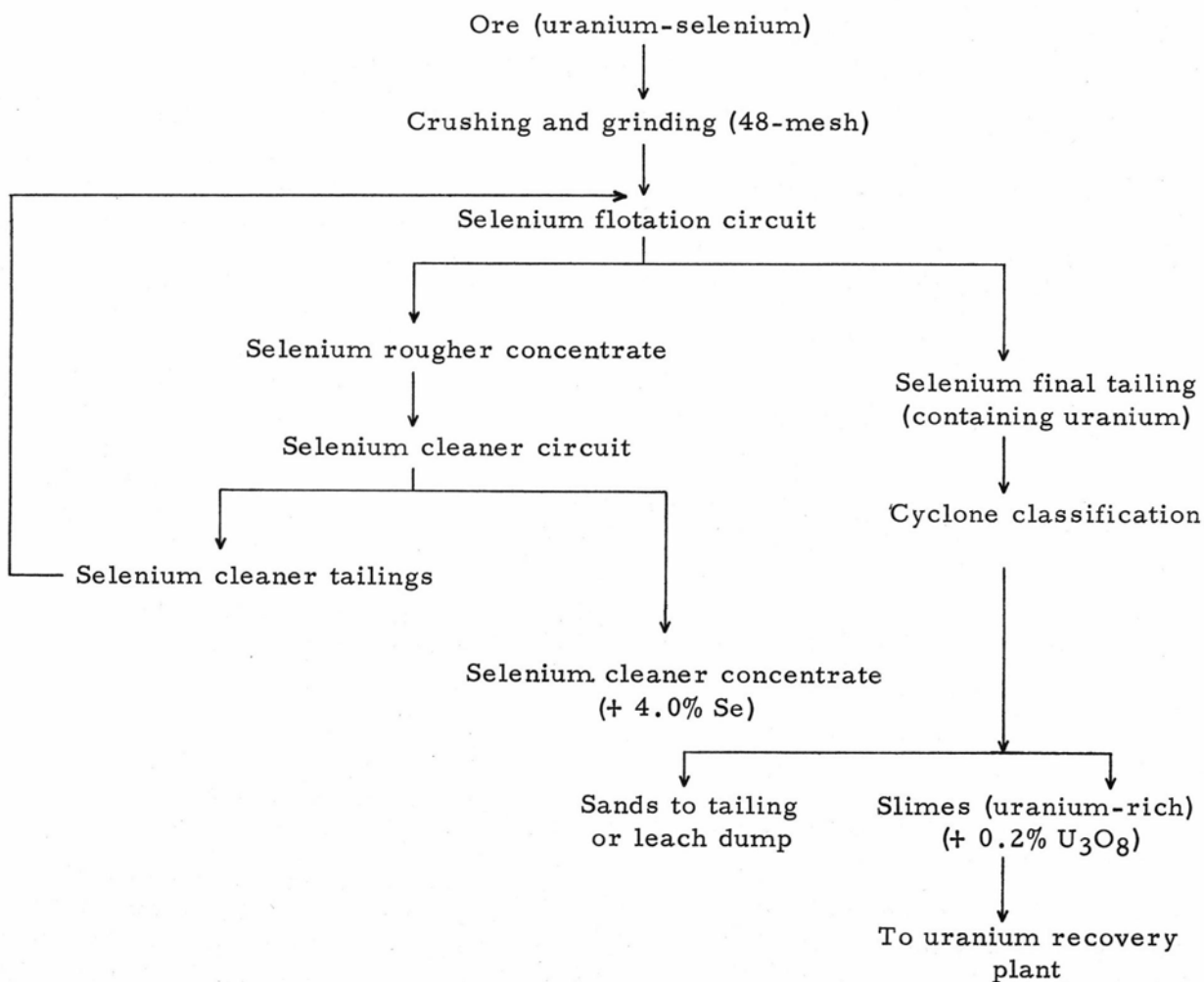
FLOWSHEET 1. TREATMENT OF URANIUM-SELENIUM ORES

Submarginal Uranium Ores Containing Selenium

In the case of low-grade uranium ores containing economically sufficient quantities of selenium, it may be possible to lower the cutoff grade for uranium in the ore below the present 0.2 percent, if selenium can be recovered as a byproduct. Under these conditions, it may be possible to treat uranium ores containing as low as 0.05 percent uranium.

After selenium flotation, in many cases, there is the possibility of upgrading the uranium content in the uranium plant feed by mechanical means.

Since in such cases the low-grade ores contain uranium minerals in the form of crusts and coatings of carnotite, coffinite, uranitite, and the like on gangue minerals, such minerals tend to be liberated during the grinding stage and to concentrate in the finer sizes in the selenium flotation feed, and subsequently in the selenium tails. On classification of the tails, preferably in cyclones, a uranium-rich overflow, amounting to about 25 to 45 percent of the total weight, is obtained. The overflow is then settled or filtered and sent to the uranium recovery plant. The coarse tails from cycloning are discarded, or stockpiled for further treatment for the recovery of the remaining uranium by heap or dump leaching.

The following flowsheet represents the treatment procedure in the case of low-grade uranium ores.

Ore (uranium-selenium)
↓
Crushing and grinding (48-mesh)
↓
Selenium flotation circuit

Selenium rougher concentrate
↓
Selenium cleaner circuit

Selenium cleaner tailings

Selenium final tailing
(containing uranium)
↓
Cyclone classification

Selenium cleaner concentrate
(+ 4.0% Se)

Sands to tailing
or leach dump

Slimes (uranium-rich)
(+ 0.2% U_3O_8)
↓
To uranium recovery
plant

FLOWSHEET 2.   TREATMENT OF SUBMARGINAL URANIUM ORES
CONTAINING SELENIUM

Uranium-Selenium -Molybdenum Ore s

During the flotation test work on sandstone ores from the Morrison formation, some of the ores tested contained appreciable amounts of molybdenum along with uranium and selenium. The molybdenum in such ore samples was present in the form of ilsmannite (probable formula: $MoO_3. SO_3 \cdot 5H_2O$), a water-soluble product also referred to as "moly blue. "

In such cases, in addition to selenium and uranium, it should be possible to recover molybdenum, which goes into solution during the grinding and selenium-flotation stages. Thus, after the flotation of selenium, the tailings can be decanted or filtered, and molybdenum recovered from the pregnant solution by suitable means. The washed solids or filter cake then would constitute uranium plant feed.

In case some of the molybdenum in the ore. occurs in non-water-soluble form, it could be leached by sodium hypochlorite, which has been found to be a strong lixiviant for molybdenum compounds. The hypochlorite must be added after selenium flotation since it has a depressing effect on such flotation.

Flotation of Carbonaceous Material

In most of the sandstone ores, some carbonaceous material is usually present, commonly containing uranium. Since such material possesses a nonpolar surface, it tends to float along with selenium, especially if kerosene or some hydrocarbon oil is present in the pulp. This can be a serious problem if considerable amounts of uranium are tied up in the carbonaceous material. In such cases, the carbonaceous material can be prevented from appearing in the flotation concentrate by the judicious use of reagents. Omission of kerosene and the use of starvation amounts of xanthates and frother help considerably in keeping down the carbonaceous material.

Other remedies available for obtaining uranium-free selenium concentrates are: (a) flotation of bulk selenium-carbonaceous material concentrate, followed by selective flotation of carbonaceous material by depressing the selenium minerals with lime, cyanide, sodium sulfide, hypochlorite, or boiling; (b) depression of selenium minerals by the above-named depressants prior to the flotation of the carbonaceous material; (c) bulk flotation of selenium-uranium concentrate, followed by carbonate leaching of uranium.

In the case of the sandstone ores investigated, the uranium content ranged from trace amounts to as high as 0.235 percent U_3O_8. Some carbonaceous material containing uranium was present in all these ores, Sandstone ores Nos. 1 and 2, especially, contained appreciable amounts of uranium-bearing carbonaceous material. Analysis of the flotation products derived

from these ores indicated, however, that less than 10 percent of the total uranium content was present in the cleaner selenium concentrates. The amount of carbonaceous material floated represented only a small fraction of the total present in the flotation feed.

DISCUSSION OF RESULTS

The results of the flotation tests for the recovery of selenium from the sandstone ores of the Morrison formation and the Galisteo formation (Dial ores)indicate that these ores are amenable to flotation procedure. Recoveries above 85 percent and acceptable grades of selenium concentrates above 4 percent are produced by a comparatively simple flotation procedure.

The flotation of native selenium and selenides with a neutral hydrocarbon oil, such as kerosene, and a sulphydryl collector, such as a xanthate, is positive and fast. The flotation of selenium is very selective, as indicated by the ratio of concentration ranging from 40:1 to 160:1. As expected, the cleaner concentrates obtained for low-grade ores are below the acceptable grade of 4 percent selenium; owing to the insufficient load in the cleaner circuit. This shortcoming is overcome, however, by increasing the load in the cleaner flotation.

For optimum results, the preparation of the flotation feed and conditioning prior to flotation are important steps in the process. Since the selenium is liberated at a 48-mesh grind with scrubbing action and the types of ore tested tend to slime badly, a rod-mill grind is ideal for these ores. Conditioning with sodium silicate, as a gangue and slime depressant, is desirable for sandstone ores; in the case of the Dial ores, such conditioning for longer periods is imperative, owing to the presence of excessive amounts of limonitic slime in the ore.

PRACTICAL APPLICATIONS OF THE PROCESS

The flotation test work and the results of the present investigation have shown that the recovery of selenium from low-grade ores as a byproduct or as a major product is practicable. The flotation procedure is relatively simple, and the reagents used are common, inexpensive, and commercially available.

Furthermore, the flotation procedure for the recovery of selenium as a byproduct of uranium mining can be incorporated easily into the existing flowsheets of the uranium reduction plants. Alternatively, the recovery of selenium can be undertaken at the mine, and the tailings from the selenium flotation circuit can be sent to the reduction plant for the recovery of uranium and other metals. The flotation procedure for selenium recovery does not interfere in any way with the subsequent extraction of uranium from the ore. On the contrary, it is logical and profitable to remove the selenium liberated in the grinding step of the uranium-extraction flowsheet.

In the case of submarginal uranium ores, the byproduct recovery of selenium may make such ores economically acceptable. Moreover, there is a good possibility of concentrating, by mechanical means, the uranium values liberated in the grinding step of the selenium-flotation flowsheet to obtain a uranium-rich product acceptable to the uranium reduction plants.

Thus, the recovery of selenium from sandstone ores by froth flotation, wherever possible, is not only economically desirable but also necessary as an incentive for the exploitation of submarginal and low-grade ores of other metals, such as uranium.

ECONOMICS OF SELENIUM RECOVERY BY FLOTATION

Consideration having been given to the technological aspect of the recovery of selenium by flotation, an attempt will be made to evaluate the process from an economic viewpoint. Only rough estimates of operating costs can be made without special study of each individual case, as such costs are determined largely by local conditions that are peculiar to the situation in question. The estimated operating costs given in this report are intended, therefore, to serve as economic guides rather than as representative of the actual costs involved. Inasmuch as the costs and economics of operation vary considerably, depending upon whether selenium is extracted from ores as the only valuable constituent or is extracted as a byproduct of some other mining operation, these two cases will be evaluated separately.

Selenium Recovered as the Major

Product Estimated Mining Costs

The mining costs included in this evaluation are the average expenses currently incurred in such operations and include overhead items, such as

amortization, insurance, and taxes. On a 500-ton-per-day operation, the estimated mining costs are $1. 50 per ton of ore produced by open-pit operations and $10. 00 per ton of ore produced underground.

Estimated Milling Costs

Based upon the data obtained from the preliminary testing, the operating expenses of a 500-ton-per-day flotation plant for treating selenium ores are estimated at about $2.50 per ton of ore treated. This figure, although it may appear low, is realistic for the treatment of selenium ores, which are relatively soft. Such ores invariably cut down the major cost of crushing and grinding, and consequently the total milling cost.

The estimated milling cost of $2. 50 per ton of ore treated is broken down as follows:

Operation and maintenance (crushing, grinding, power, etc.)	$0. 50
Reagents and supplies	0. 20
Labor	0. 80
Overhead (amortization, insurance, taxes, etc. , calculated over a 5-year period)	1. 00
Total mill operating cost per ton of ore treated	$2, 50

Estimated Total Operating Costs

On the basis of the above estimates of the mining and milling costs for selenium ores, the following total operating costs are suggested: (a) for open-pit operations and milling, $4. 00 per ton; (b) for underground operations and milling, $12. 50 per ton.

Determination of Cutoff Grades

The cutoff grades are computed on the basis of the following factors:

1.   Values of $4. 00 and $12. 50 for open-pit and underground mining operations respectively, as the minimum return per ton of ore for breaking even.
2.   A flotation recovery of 85 percent of the total selenium content of the ore.
3.   A price for selenium concentrates of $6. 00 per pound of contained selenium, computed on the basis of 86 percent of the current market price of selenium metal ($7. 00 per pound).
4.   A 500-ton-per-day mining and milling operation.

The approximate cutoff grades calculated on the basis of the above factors are (a) for open-pit operations and milling, 0. 04% Se; (b) for underground operations and milling, 0. 12% Se. These estimated cutoff grades represent the minimum grades for breaking even when selenium is the only major constituent recovered from the ore. These cutoff grades would vary with the size of the ore body, prothiction capacity, price of the metal, and metallurgical efficiency.

Selenium Recovered as a Byproduct

In the case of the flotation recovery of selenium as a byproduct of mining for some other valuable metal, such as uranium, a different economic picture is presented. In such instances, the operating costs for mining, as well as for the major part of milling, such as crushing and grinding, already are accounted for in the economics of the major product extracted from the ore. The only additional cost involved is the expense of floating selenium. Inasmuch as the more expensive milling operations, such as crushing and grinding, are charged to the cost of recovering the major product, the total milling cost for selenium would be reduced considerably and should not amount to more than $1.00 per ton of ore treated. This estimate, applicable to a 500ton-per-day flotation plant, is broken down as follows:

Operation and maintenance	$0. 15
Reagents and supplies	0. 20
Labor	0.40
Overhead (calculated over a 5-year period)	0. 25

Total milling operating cost, per ton of ore treated $1. 00

Cutoff Grade for Byproduct Selenium Recovery

On the previously considered basis of 85-percent flotation recovery and a price of selenium concentrates of $6.00 per pound of contained selenium, the cutoff grade for a break-even return value of $1. 00 per ton of ore treated is computed to be approximately 0. 01 percent selenium.

This cutoff grade of 0. 01 percent selenium for byproduct recovery of the metal from various ores, such as those of uranium, is frequently encountered in current mining operations. A selenium content in such ores above the cutoff grade of 0. 01 percent deserves attention.

CONCLUSIONS

The following conclusions are drawn from the present investigation concerning the flotation recovery of selenium from sandstone ores found in New Mexico.

1. The selenium in the sandstone ores from the Morrison and Galisteo formations occurs as native selenium (mostly of the gray variety) and (or) as selenides, especially ferroselite (iron selenide). Two other minor minerals that contain some selenium are: (a) an unidentified reddish mineral containing lead and molybdenum in addition to selenium, and (b) some massive pyrite s.

2. The selenium content in the sandstone ores from the Morrison formation varies from a trace amount to as high as 0.432 percent, whereas the Dial ores from the Galisteo formation contain about 0.032 percent selenium.

3. Selenium-bearing sandstone ores are amenable to simple flotation procedures for the recovery of selenium in the form of acceptable grades of selenium concentrates.

4. Proper preparation of the samples prior to flotation consists of a 48-mesh rod-mill grind followed by thorough conditioning with a slime and gangue depressant, such as sodium silicate. Care is required in the grinding step to avoid overgrinding of the sample.

5. For Dial ores containing excessive limonitic slimes, proper sample preparation and conditioning are imperative for successful flotation. In such cases, rod-mill grinding of the plus-48-mesh product remaining after thorough agitation in the Fagergren flotation machine, and conditioning with larger amounts of sodium silicate for a prolonged conditioning time, are essential.

6. The flotation reagents required for selenium flotation are 1. 0 pound of soda ash, 1.5 to 2.5 pounds of sodium silicate, 0.1 pound of kerosene, 0.05 pound of potassium amyl xanthate, and 0.1 pound of Dow Froth 250, per ton of ore treated.

7. The flotation of selenium under optimum conditions is very selective and rapid. Rougher concentrates containing 0. 50 to 4. 0 percent selenium are produced, depending upon the selenium content in the feed. The flotation recovery in the rougher circuit amounts to better than 85 percent for low-grade ores and to as high as 97 percent for high-grade ores.

8. In the case of low-grade ores,. the cleaning of the rougher concentrates is necessary for obtaining acceptable grades above• 4. 0 percent selenium. For high-grade ores, cleaner concentrate grades as high as 16 percent are obtainable by a single cleaning. With two or more cleanings, it is possible to obtain grades above 50 percent selenium.

9.   Economic evaluation of the flotation recovery of selenium from sandstone ores indicates that for recovery of selenium as the only valuable product of such ores, the break-even cutoff grades are approximately 0.04 and 0.12 percent selenium for open-pit and underground mining operations respectively.

10. When selenium is recovered as a byproduct of some other mining operation, such as uranium, the cutoff grade for breaking even is reduced to about 0.01 percent selenium. Therefore, currently mined uranium ores containing more than 0.01 percent selenium should be worthy of further investigation for the economic recovery of selenium as a byproduct. Moreover, byproduct recovery of selenium should make profitable the exploitation of low-grade uranium ores containing less than 0.2 percent U_3O_8.

11. The recommended flowsheet for the byproduct recovery of selenium by flotation can be easily incorporated into the existing uranium-extraction flowsheets.

ACKNOWLEDGMENTS

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