CONCRETE
Information

Ettringite Formation and the Performance of Concrete

In the mid-1990's, several cases of premature deterioration of concrete pavements and precast members gained notoriety because of uncertainty over the cause of their distress. Because of the unexplained and complex nature of several of these cases, considerable debate and controversy have arisen in the research and consulting community. To a great extent, this has led to a misperception that the problems are more prevalent than actual case studies would indicate. However, irrespective of the fact that cases of premature deterioration are limited, it is essential to address those that have occurred and provide practical, technically sound solutions so that users can confidently specify concrete in their structures.

Central to the debate has been the effect of a compound known as ettringite. The objectives of this paper are:

- to define ettringite and its form and presence in concrete,

- to respond to questions about the observed problems and the various deterioration mechanisms that have been proposed, and

- to provide some recommendations on designing for durable concrete.

Because many of the questions raised relate to cement characteristics, a brief primer on cement manufacture and chemistry is included in Appendix A.

What Is Ettringite?

Ettringite is the mineral name for calcium sulfoaluminate ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), which is normally found in portland cement concretes. Calcium sulfate sources, such as gypsum, are intentionally added to portland cement to regulate early hydration reactions to prevent flash setting, improve strength development, and reduce drying shrinkage. Sulfate and aluminate are also present in supplementary cementitious materials and admixtures. Gypsum and other sulfate compounds react with calcium aluminate in the cement to form ettringite within the first few hours after mixing with water. Most of the sulfate in the cement is normally consumed to form ettringite at early ages. The formation of ettringite in the fresh, plastic concrete is the mechanism that controls stiffening. At this stage ettringite is uniformly and discretely dispersed throughout the

Fig. 1. Portland cements are manufactured by a process that combines sources of lime (such as limestone), silica and alumina (such as clay), and iron oxide (such as iron ore). Appropriately proportioned mixtures of these raw materials are finely ground and then heated in a rotary kiln at high temperatures, about 1450 °C (2640 °F), to form cement compounds. The product of this process is called clinker (nodules at right in above photo). After cooling, the clinker is interground with about 5% of one or more of the forms of calcium sulfate (gypsum shown at left in photo) to form portland cement. The calcium sulfate controls setting time, strength development, and drying shrinkage potential.

cement paste at a submicroscopic level (less than a micrometer[1] in cross-section).

Ettringite formed at early ages is often referred to as "primary ettringite." It is a necessary and beneficial component of portland cement systems.

Why Does Microscopic Analysis Often Show Ettringite in Concrete?

It has been known for many years that if concrete is exposed to water for long periods of time, primary ettringite can slowly dissolve and reform in any available voids or microcracks [Lerch, 1945]. This is why, under microscopic examination, needle-like crystals of ettringite are often observed lining air voids or cracks in older concretes, including those from structures that have demonstrated a high level of durability.

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[1]A micrometer is one millionth of a meter, which is about 0.00004 in.
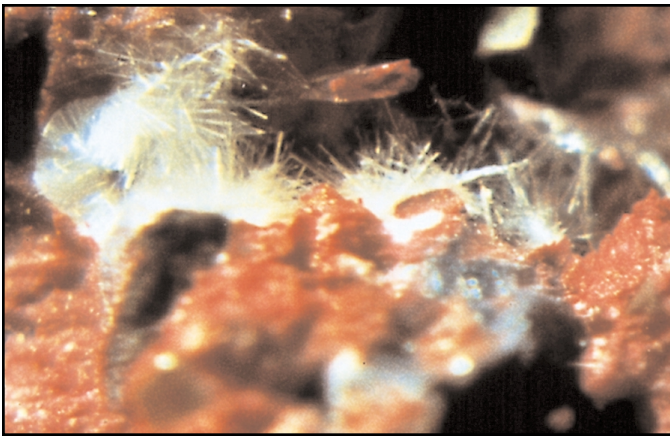
Fig. 2. Ettringite (white, needle-like crystals) are commonly found in samples taken from concrete in service, especially in concrete from moist environments. Secondary ettringite is not detrimental to concrete performance. [Concrete in photo exposed to phenolphthalein stain to highlight features.]

Any deterioration of concrete by freeze-thaw action, alkali-silica reactivity (ASR), or other means, accelerates the rate at which ettringite leaves its original location in the paste to go into solution and recrystallize in larger spaces such as voids or cracks. This is because both water and space must be present for the crystals to form. The space can be provided by cracks that form due to damage caused by frost action, ASR, drying shrinkage, thermal gradients, or other mechanisms. In addition, deterioration caused by such mechanisms provides greater surface area of exposure and easier paths for ingress and egress of water.

Ettringite crystals in air voids and cracks are typically 2 to 4 micrometers in cross-section and 20 to 30 micrometers long. Under conditions of extreme deterioration, and repeated wetting and drying, ettringite crystals can appear to completely fill voids or cracks. However, ettringite, found in this benign state as large needle-like crystals, should not be interpreted as causing the expansion of deteriorating concrete.

To confirm that ettringite does not contribute to expansion of deteriorating cast-in-place concrete, Lerch investigated effects of cement sulfate levels on alkali-silica reaction and freeze-thaw action [Lerch, 1945]. By using cements of different sulfate contents (higher sulfate contents having potential to form more ettringite), he evaluated whether the solution and recrystallization of the calcium sulfoaluminate contribute to expansion.

The ASR study used a reactive aggregate with cement alkalies ranging from 0.53% to 1.05% Na_2O equivalent. Mortar and concrete prisms were tested beyond three years. Concrete prisms were exposed to field and laboratory conditions. Specimens with the 3.5% sulfate cements usually had about the same, and often less, expansion than those with the 1.5% sulfate cements. This indicates that expansion in the specimens resulted from ASR, and recrystallization of the ettringite, occurring in spaces created by the ASR, did not contribute to the expansion.

The freeze-thaw study tested concretes with cements having sulfate contents ranging from 1.7% to 4.0%. The specimens were exposed to 160 freeze-thaw cycles, followed by 28 days of

drying in air, followed by one year in water. This testing regimen theoretically would disrupt the paste and provide a dry and then wet environment ideal for the recrystallization of ettringite. The specimens prepared with the cements with 4.0% sulfate had less expansion and a smaller decrease in dynamic modulus than those with lower sulfate content. No abnormal expansion was observed after the water storage. This indicates that the expansion in the specimens resulted from frost damage and not from recrystallization of ettringite. This research did not investigate the hypothesis that partial or total void filling by ettringite could reduce the protection the air void system affords against freeze-thaw damage (see discussion of freeze-thaw resistance below).

Ettringite formed by dissolution and recrystallization in void spaces and cracks is often referred to as "secondary ettringite." Secondary ettringite is not detrimental to concrete performance.

Can Excess Soluble Sulfates in Cement Cause Deleterious Expansions in Concrete?

If inordinately high amounts of gypsum (or other sources of calcium sulfate) are added to cement, and if concrete made with that cement is in a moist service environment, deleterious expansions can occur. Sulfates from gypsum or other forms of calcium sulfate used to control properties of cement are readily soluble and react soon after cement comes into contact with mix water. However, if extremely high levels of gypsum are added, abnormal expansions can occur from excessive calcium sulfoaluminate formation after hardening and continuing until the gypsum becomes depleted. This was demonstrated by Lerch in 1945; he showed that gypsum additions to give cement SO_3 contents of up to 5.0% had no significant impact on expansion of mortar bars stored in a moist room. However, when inordinately high gypsum levels (up to 7.5% as SO_3) were added to clinker, excessive expansions were generated. The rate of length changes in the mortar bars showed that most of the expansion took place
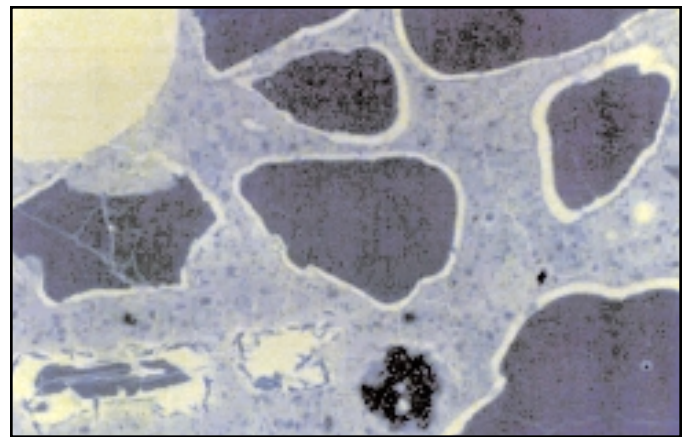

Fig. 3. This is a photomicrograph of a mortar sample that had been stored in water for six years at 20 °C. To simulate an over sulfated system, part of the sand was replaced by gypsum, and thus significant expansions occurred. Note that the gaps around the sand grains in the mortar are similar in appearance to those observed for delayed ettringite formation.

within three months. This implies that if excessive soluble sulfate contents in cements were available, it would be reasonable to expect field problems in concrete made from that cement to show up relatively early in the life of the structure, probably within the first six months. Commercially produced portland cements in the U.S. contain less than 5% SO_3.

The potential impact of excessive gypsum has thus been known for some time, and is the reason ASTM C 150, *Standard Specification for Portland Cement* contains provisions for control of sulfates in portland cement. Using requirements of ASTM C 150, one can optimize the level of sulfates in cements to maximize strength and/or minimize shrinkage, without excessive expansion potential. Cements are optimized prior to production by testing at various sulfate levels to achieve maximum strengths in mortar cubes (and/or minimum shrinkage of mortar prisms). ASTM C 150 contains numerical limits on sulfate levels that are a function of cement type. In cases where the optimum sulfate level exceeds table limits, the standard includes an option for a performance test that measures expansion of mortar bars stored in water. This provides the opportunity to optimize cements for sulfates, while protecting against the potential for deleterious expansions.

Can Ettringite Formation Reduce the Freeze-Thaw Resistance of Concrete?

One hypothesis that has been considered to explain premature damage observed in pavements is that the protective air entrainment system has been rendered ineffective because of ettringite filling of air voids. The theory is that increased sulfate levels within the concrete, from excess sulfates in cement or fly ash, result in an excessive level of ettringite that clogs the entrained air void system. A related hypothesis is that external sources of sulfates, as found for example in gypsum in deicing salts, could increase susceptibility to freeze-thaw damage. These hypotheses have appeal. Theoretically, if even one ettringite crystal were to form in an air void, the volume of air void space would be reduced. However, the question remains as to whether there could be sufficient infilling to harm properly air-entrained concrete, which would have a paste system with air voids well in excess of those needed to accommodate volumetric expansion of water during freezing.

A series of laboratory tests were undertaken to test these hypotheses [Detwiler and Powers-Couche, 1997]. Three cements produced from the same raw materials were used. Two were commercial Type I (C_3A=12%; SO_3=2.03%) and Type II (C_3A=5%; SO_3=2.72%) cements; the third was made by intergrinding the Type I cement with additional gypsum (SO_3=3.14%) to increase the amount of available sulfate in the concrete. Concrete prisms made from these cements were subjected to freezing and thawing under conditions outlined in ASTM C 666 Procedure A, except that 3% NaCl solutions either with or without added gypsum (to simulate road salt) were used instead of water. In addition, freeze-thaw cycles were interrupted over weekends to simulate a wetting and drying environment, an exposure conducive to ettringite crystal growth. Air contents originally selected for test were 2±0.5%, 4±0.5%, and 6±0.5%.

However, after over 300 cycles, the 6% air specimens were discontinued, as no deterioration was observed. Thus, the remaining tests were conducted on marginal to poor air content concretes. Specimens were tested to destruction in most cases. Periodically during the testing, companion specimens were evaluated petrographically to evaluate ettringite formation in voids.

Conclusions from this study were that performance of the concretes was dominated by the quality of the air void system. For non-air-entrained concrete (2%), damage occurred without formation of ettringite deposits. For marginally air-entrained concrete (4%), deposition of ettringite appeared to follow the formation of cracks as freeze-thaw deterioration occurred. Ettringite did not cause the cracking, nor did it contribute to the propagation of existing cracks. Cracks due to frost damage created space for ettringite crystals to grow. Also, the presence of gypsum in the salt solution had no significant effect on the test results. The governing factors in performance of the specimens were the volume of air and quality of the air void system in the hardened concrete.

Subsequent to the above program, a second program was initiated to test two cement systems at higher sulfate levels [Taylor, 1999]. One cement (labeled A in figs. 4-6) had a sulfate level of 4.04% (clinker sulfate was 1.9%). The other cement had a sulfate level of 2.78% (clinker sulfate was 0.39%), but prior to testing, gypsum was intentionally added to reach a cement sulfate level of 4%. Concretes were made from each cement and tested under the modified ASTM C 666 as described above, but using only the 3% NaCl solution with added gypsum. The fresh concretes had entrained air contents of 5.5% and 5.9%, with a good air void distribution as measured on the hardened concretes. Results exceeded commonly applied performance requirements at 300 cycles (relative dynamic modulus greater than 90%), so testing was continued to 900 cycles. Conclusions were that ettringite was observed to have formed in voids near the surface, but was not related to the observed deterioration of the specimens at later cycles. Performance was a function of the quality of the air void system.

Both studies once again confirm the need for properly air-entrained concrete in structures exposed to severe freeze-thaw environments.

Are There Slowly Soluble Sulfates in Cement Clinker That Can Result in Late-Forming Ettringite and Subsequent Deleterious Expansions in Concrete?

The hypothesis for a deterioration mechanism related to slowly soluble sulfates is that some portions of the sulfates in clinker are in a form that is very slowly soluble or are incorporated in the silicate phases such that they are not available to participate in early hydration reactions. The slowly soluble form has been attributed to the potential presence of β-anhydrite,[2] $CaSO_4$ (see Appendix A).

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[2] ß-anhydrite is often referred to as "hard burned" anhydrite, which is a term used in the gypsum plaster industry. It is commonly misperceived that ß-anhydrite is "insoluble." However, while its rate of solubility is less than other forms, it is sufficient to act as an effective set controller [Hansen et al., 1988, and Michaud and Suderman, 1999]
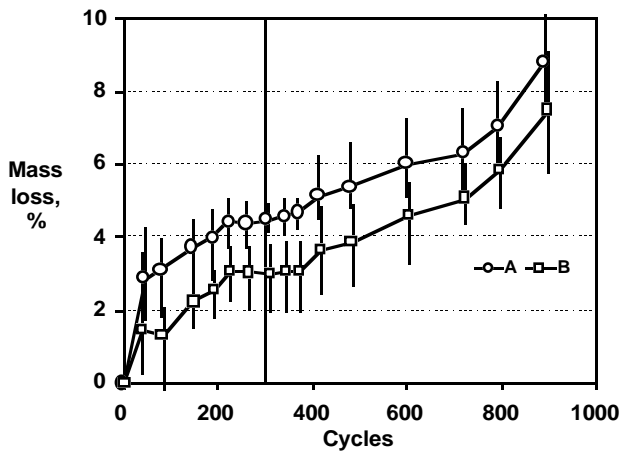
Fig. 4. Mass loss of concrete samples subjected to modified ASTM C 666 cycling (after Taylor 1999)
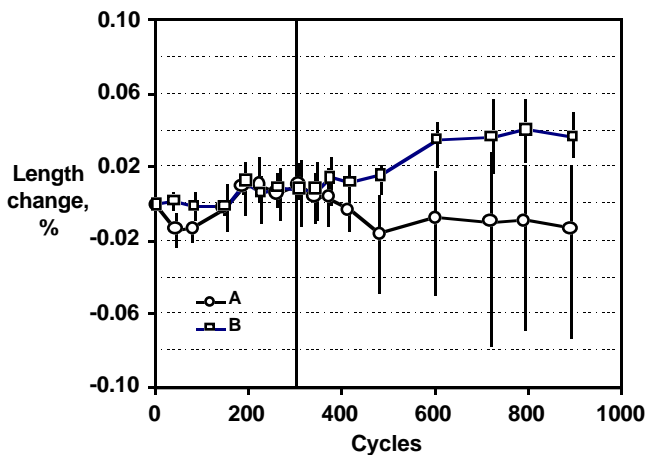

Fig. 5. Length change of concrete samples subjected to modified ASTM C 666 cycling (after Taylor 1999)
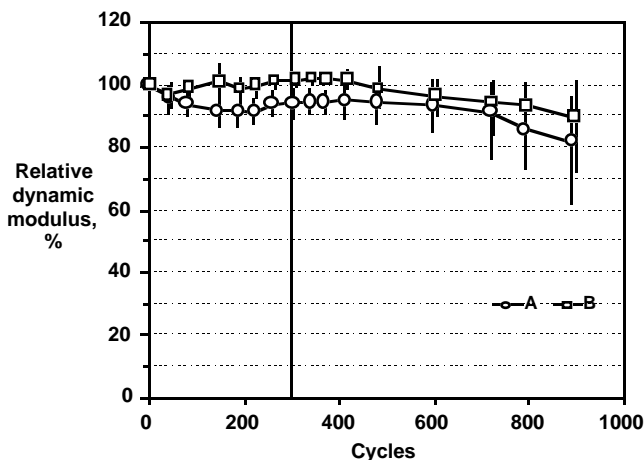

Fig. 6. Relative Dynamic Modulus of concrete samples subjected to modified ASTM C 666 cycling (after Taylor 1999)

The implication of the hypothesis regarding sulfates incorporated in the silicate phases is that some of the silicates, particularly belite (C_2S), do not hydrate until after initial hardening; thus, the "trapped" sulfates would only become available to form ettringite after concrete has hardened, assuming available moisture.

The potential for slowly soluble sulfates in clinker has been associated with increased levels of total clinker sulfate. The concern expressed is that changes in cement manufacturing technology (changes in fuels, recycling of cement kiln dust—CKD—or use of alternative fuels such as tires) have resulted in increased levels of sulfates and the potential for slowly soluble sulfates. Concern has also been expressed that moving from wet process production to dry process and preheater, precalciner systems has increased potential for sulfates in alite and belite.

Changes have occurred in cement manufacture with movement toward more energy efficient dry process production and environmental controls. There are four primary types of kiln systems: wet, long dry, preheater, and precalciner. The latter three are dry process systems that do not use a water slurry of raw materials. The preheater and precalciner are the most energy efficient kiln types, and generally are newer. However, dry process kilns have been used for many years (Appendix A). There is no basis to assume that the kiln system in itself would govern sulfate levels or potential for slowly soluble sulfate.

On average, clinker sulfate levels have increased.[3] The change from natural gas to coal as a fuel source, which the industry made as a result of the energy crisis of the early 1970s, led to some increase. Also, since the original Clean Air Act in the 1970s mandated collection systems for particulate emissions, there has been a relative increase in CKD available as a raw material source. CKD is composed of fine particles that consist predominantly of partially calcined forms of the original raw materials introduced into the kiln [Klemm, 1994]. CKD also contains alkali sulfates, which are incorporated into the dust as they volatilize off the kiln feed during calcination. Relative to cement performance, alkali sulfates react readily during early hydration reactions. Reuse of CKD varies from plant to plant because of kiln operating conditions. In addition, since CKD can contribute to increased alkali levels of cement, the amount that can be used as a raw feed source may be limited.[4] It should also be noted that recycling of CKD as kiln feed is not new or unique. It has been a normal, environmentally beneficial operating practice in many plants worldwide. In fact many plants in the U.S. recycle all of their CKD, without detriment to the final product. There are no data to indicate that CKD use as a raw material contributes to potentially detrimental slowly soluble sulfates, nor is there any identified relationship between CKD use as raw feed in cement manufacture and observed field problems with concrete made from that cement.

Questions have also arisen regarding use of alternative fuels such as liquid solvents or tires. Liquid solvents are normally lower in sulfur than the fuel they replace. Published data on sulfur in tires indicate a range from about 0.9% to 1.8% by mass, with an

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[3] See Appendix A.

[4] Contrary to a perception often expressed, CKD use as a raw material is not the primary source of cement alkalies. Alkali levels in cement are strongly dependent on the alkali content of the original raw materials.

average of 1.3%. Data for coal indicate a range of about 0.3% to 4.0%, with an average of 1.5%. Tires have about a 20% higher Btu value than coal. Given the fact that tires only replace about 10% to 20% of conventional fuel Btu value, they have little impact on overall sulfate levels in clinker. It should also be recognized that there is no identified relationship between the problems encountered in field concretes and cement sourced from plants using alternative fuels.

The hypothesis that clinker sulfates are slowly soluble has been criticized on the basis that the dominant form of sulfate in clinker, alkali sulfates, are in fact rapidly soluble, as are the forms of calcium sulfate added to make portland cement: gypsum, hemihydrate, and anhydrite. Michaud and Suderman (1999) have demonstrated that even anhydrite is sufficiently soluble to act as a set control agent as it dissolves and reacts quickly. The amount of calcium sulfate added to the mill with the clinker to control cement setting is adjusted to account for sulfates present in clinker.

To evaluate the hypothesis regarding slowly soluble clinker sulfates, a study of 33 commercially available clinker samples was undertaken [Klemm and Miller, 1997]. The SO_3 contents ranged from 0.03% to 3.00% by mass. The sample population was skewed toward higher (> 1.5%) SO_3 clinker, since these were of most interest and were specifically requested for the voluntary testing program. The samples also represent current conventional manufacturing practice for all four kiln system types. The molar SO_3/Na_2O_{eq} of the clinker samples ranged from 0.06 to 2.54, which is representative of a broad range of production. This ratio is of interest because it indicates the balance of sulfates and alkalies in the system (alkali sulfates are rapidly soluble). The samples were evaluated by selective dissolution techniques. The objective was to determine the form and distribution of the sulfates. The selective dissolution technique works by using a potassium hydroxide/sugar solution to dissolve non-silicate (interstitial) phases and then evaluating the sulfates in the residue left after extraction. The residue is then further dissolved in salicylic acid/methanol solution to remove the silicates, and the remaining residue is evaluated for sulfates. This allows differentiation of sulfates in the silicate phases from the interstitial phases. In addition, the form of sulfates in the phases can be evaluated by X-ray diffraction.

No β-anhydrite was found in the samples. Also, only small amounts of sulfate were found to be incorporated in the silicate phases; this distribution did not correlate with the total measured sulfate. Thus, the tests indicate that only very minor amounts of clinker sulfate appear to remain after the first day of hydration. In no case did this represent more than 0.85% in the silicates or 0.68% for the clinker as a whole. For clinker sulfate incorporated in silicate phases, the amount of SO_3 potentially available for possible late reactions to form ettringite was balanced by an equal or greater amount of alumina, thus making the formation of ettringite unlikely, as three times more SO_3 than alumina is required to form ettringite. If SO_3 and alumina are balanced, monosulfoaluminate would be expected to form.

This work has been extended to include expansion tests of mortar bars made from the cements of the test clinker samples and subjected to moist storage conditions [Tennis et al., 1999, and Olek and Zhang, 1999]. These tests were undertaken to confirm the levels of expansion that could occur at the known amounts and distribution of clinker sulfate. Results of the mortar bar expansion measurements show that, for curing temperatures below 70 °C (158 °F), no excessive expansions have occurred, even when excess gypsum was added to give cement sulfate levels one percent above optimum.

The selective dissolution tests indicate that clinkers manufactured in accordance with conventional industrial practices do not contain slowly soluble sulfates that could cause cements to induce deleterious expansions in concretes. Review of the literature on this topic supports this finding [Taylor, 1996]. Analytical methods using selective dissolution are available to verify the form and distribution of sulfates in clinker.

What About Delayed Ettringite Formation due to High Temperatures?

It has been known for some time that concrete subjected to early-age temperatures high enough to destroy some or all of the ettringite originally formed can, in the presence of moisture, undergo deterioration with the reformation of ettringite in the hardened paste system [Day, 1992; Famy, 1999]. The term "delayed ettringite formation" (DEF) is commonly used to refer to the potentially deleterious reformation of ettringite in moist concrete, mortar, or paste after destruction of primary ettringite by high temperature. Such early-age temperatures may result from heat treatment, or in extreme cases, from internal heat of hydration.

The temperature conditions for deleterious expansion due to DEF have not been conclusively defined. However, a heat treatment temperature above about 70 °C (158 °F) is most often cited [Taylor, 1994]. This temperature is affected by factors such as moisture conditions during heat treatment, cement characteristics, the concrete mix, and interactive effects of other deterioration mechanisms, such as alkali-silica reactivity, and freezing and thawing.

Based on laboratory testing of mortar prisms, deleterious expansions have not been observed at temperatures of 70 °C (158 °F) or less, irrespective of cement characteristics. At increasing maximum temperature levels above 70 °C (158 °F), factors such as cement characteristics begin to have an impact [Kelham, 1999].

Based on laboratory tests of mortars, Kelham identified characteristics of cement that show increased sensitivity to heat treatment [Kelham, 1997 and 1999]. When cured at temperatures above 90 °C (194 °F) the following characteristics of cement led to greater expansions in mortars subjected to extended periods (5 years) of moist curing:

- Higher fineness

- Higher C_3A

- Higher C_3S

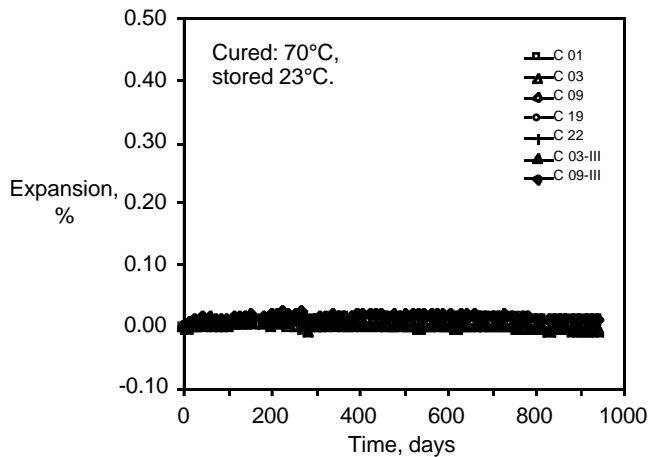- Higher alkali (Na_2O_{eq})

- Higher MgO.

Fig. 7. For a range of cements, including those that would be considered at high risk, no deleterious expansions have been observed in mortar bars cured at 70 °C.
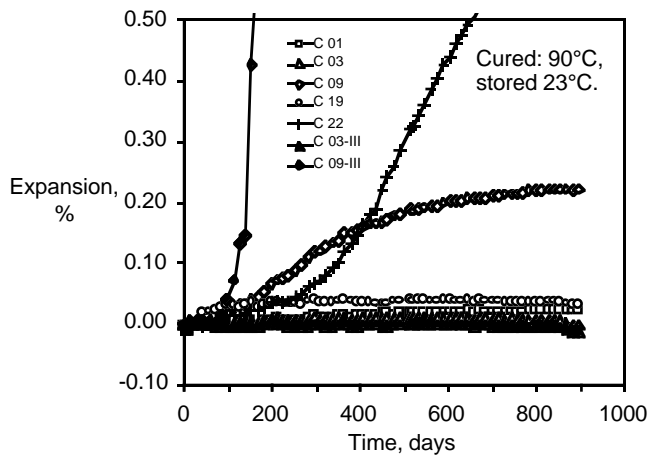

Fig. 8. When cured at 90 °C, some mortar bars show significant expansions after about 100 days.

Cements with high fineness, C_3A, C_3S, and Na_2O_{eq} are generally associated with higher SO_3 levels because more sulfates are required to control early stiffening. In addition, these are the same characteristics that provide increased early-age strengths and are most desirable from the perspective of rapid construction cycles. The sulfate (SO_3) to aluminate (Al_2O_3) ratio is important as, for a given C_3A content, it influences the amount of primary ettringite formed.

Another factor that is significant regarding early heat treatment of concrete is the preset or delay period prior to application of heat [Day, 1992]. Application of heat without allowance for a preset period increases susceptibility to DEF. The importance of preset time has long been established, as it also affects strength [Pfeifer and Landgren, 1982]. Control of early temperatures has become more significant with the advent of higher release strength requirements, availability of more reactive cements, high-range water reducers that permit very low water-cement ratios, and use
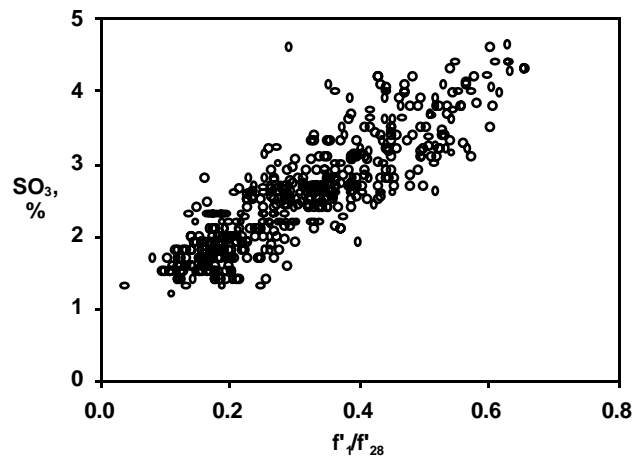

Fig. 9. Those factors that lead to higher early strengths in cement (higher fineness, C3A, C3S, and alkalies) are associated with higher sulfate (SO3) levels to control early stiffening. In this figure, the required level of cement sulfate is shown to increase with an increasing ratio of 1–28- day strengths. Both Type I and Type III cements are included in the figure.

of newer heating technologies that may impact moisture conditions during curing.

Aggregates have also been shown to have an impact on DEF, with limestone sources being preferred [Taylor, 1994]. This has been attributed to better paste-aggregate transition zone characteristics with limestone aggregates [Day, 1992]. Also, because delayed ettringite formation is very often associated with alkali-silica reactivity, the use of potentially reactive aggregates can be an exacerbating factor [Taylor, 1994].

Data have indicated that use of air entrainment reduces expansions as compared to non-air-entrained mortars [Day, 1992]. This observation is indirectly supported by the fact that there have been no reported field cases of DEF in adequately air-entrained concretes. The air entrainment does not prevent DEF, but apparently permits ettringite formation in air voids rather than in confined paste pore structure.

Supplementary cementing materials (pozzolans and slag) have also been demonstrated to reduce the potential for deleterious expansion due to DEF. However, there is not yet sufficient data to provide definitive recommendations on the levels required with different cements and curing conditions [Thomas, 1998]. While it might be assumed that use of SCMs would not be viable for high early strength requirements, there are combinations that have potential to develop early strength. For example, use of slag with reactive portland cement can provide relatively high early strengths. There is also potential for use of ternary mixtures.

Delayed ettringite formation (DEF), the reformation of ettringite after destruction of primary ettringite by high temperature, can cause premature deterioration of concrete in moist service environments. The vast majority of heat-treated concrete elements provide in-service performance well in excess of design expectations. If historical production experience indicates satisfactory performance, there does not appear to be a need to
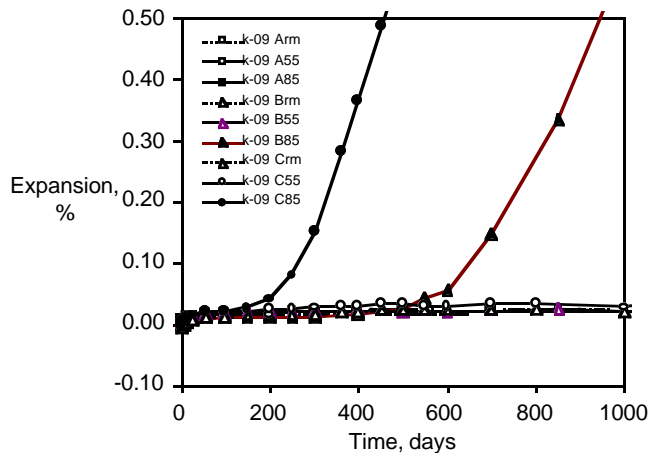
Fig. 10. Expansion measurements for mortar bars made with a particular cement at various sulfate levels. The sulfate was interground with clinker in the laboratory. The B series is at optimum sulfate; the A series is 1% below optimum, and the C series is 1% above optimum. Curing temperatures were ambient room temperature (rm), 55 °C, and 85 °C. Only those specimens cured at 85 °C have shown expansions over the first 1000 days of storage over water. Similar results have been found for other cements in this study.

change practices unless other factors, such as release strength requirements, constituent materials characteristics, mix designs, or curing practices are changed. Also, many producers in warm climates do not use externally applied heat, but depend on internal heat of hydration to achieve production cycles. Again, if experience dictates satisfactory performance, changes in practices may not be warranted. However, it would be prudent to monitor materials and production to insure no unanticipated changes occur.

The following represent measures that are recommended in the literature for heat-treated concretes:

• Provide an adequate preset or initial delay time prior to applying heat. The Precast/Prestressed Concrete Institute (PCI) recommends that the delay period be determined by testing for initial setting time in accordance with ASTM C 403, *Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance* [PCI, 1996]. German and Canadian standards recommend a minimum delay period of 1 hour at 30 °C (86 °F) for elements that will be dry in service, and 3 hr. at 30 °C (86 °F) or 4 hr. at 40 °C (104 °F) for elements that will be damp[5] in service [Deutscher Ausschuss für Stahlbeton, 1989 and CSA, 1994].

• Avoid rapid heating rates after the preset time. German and Canadian standards use 20 °C/hr. (36 °F/hr.).

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[5] CSA classifies "damp" as those elements that will be subjected to a moist environment during service or non-air entrained elements that will be exposed to a moist environment for a period of more than 3 months prior to service. This includes external elements of buildings or structures exposed to precipitation, surface water, or ground water, such as bridge girders, building facades, basement walls, railway ties, and underground vaults. Internal building elements subjected to moist conditions, such as in parking garages, would also be included, as would elements such as internal voids in bridges that are subject to condensation.

• Limit maximum temperature of the concrete during curing. German and Canadian standards use a maximum of 80 °C (176 °F) for concrete that will be dry in service, and 60 °C (140 °F) or 70 °C (158 °F), respectively for concrete that will be damp in service.

• Avoid rapid cooling rates. German and Canadian standards use 10 °C/hr. (18 °F/hr.) as the maximum rate of cooling from peak temperature.

• Specify the lowest release strengths necessary to meet design and construction requirements.

• Follow appropriate guidelines to control alkali-silica reactivity [see Farny and Kosmatka, 1997].

• Do not specify one-day cement strengths higher than required to meet production schedules.

• Use appropriate quality control to minimize the need to overdesign the concrete mix; do not use excessive cement factors to compensate for processing variations.

• Avoid moisture loss during the entire curing cycle using protective sheets or externally applied moisture.

• Avoid hot spots in localized areas.

ACKNOWLEDGMENTS

Appendix A:
A Primer on Cement

Brief Overview of Cement Manufacture[6]

Portland cement is produced by pulverizing clinker consisting essentially of hydraulic calcium silicates along with some calcium aluminates and calcium aluminoferrites and usually containing one or more forms of calcium sulfate (gypsum) as an interground addition.

Materials used in the manufacture of portland cement must contain appropriate proportions of calcium oxide, silica, alumina, and iron oxide components. During manufacture, analyses of all materials are made frequently to ensure a uniformly high quality cement.

Steps in the manufacture of cement are illustrated in the flow charts in Figs. A-1 and A-2. While the operations of all cement plants are basically the same, no flow diagram can adequately illustrate all plants. There is no typical portland cement manufacturing plant; every plant has significant differences in layout, equipment, or general appearance. Following is an approximate distribution of current cement capacity by primary kiln type:

Process type	Percent of total capacity	Avg. age (yr.)
Wet	28	36
Long dry	22	38
Preheater	21	24
Precalciner	29	14

Selected raw materials are crushed, milled, and proportioned in such a way that the resulting mixture has the desired chemical composition. The raw materials are generally a mixture of calcareous (calcium oxide) material, such as limestone, chalk, or marine shells, and an argillaceous (silica, iron, and alumina) material such as clay, shale, or blast-furnace slag. Either a dry or a wet process is used. In the dry process, grinding and blending are done with dry materials. In the wet process, the grinding and blending operations are done with the materials in aqueous slurry form. In other respects, the dry and wet processes are very much alike. Fig. A-2 illustrates important technological developments that can improve significantly the productivity and energy efficiency of dry-process plants.

After blending, the ground raw material is fed into the upper (feed) end of a rotary kiln, or into a preheater tower. The raw mix passes through the kiln at a rate controlled by the slope and rotational speed of the kiln. Burning fuel (powdered coal, oil, or gas, sometimes supplemented with alternative fuels such as tires) is forced into the lower (discharge) end of the kiln where temperatures of about 1450 °C (2640 °F) change the raw material chemically into cement clinker, grayish-black pellets predominantly the size of 13-mm (1/2-in.)-diameter nodules.

The clinker is cooled and then pulverized. During this operation a small amount of gypsum (approximately 5%) is added to regulate the setting time of the cement. The clinker is ground so that most of it passes through a No. 325 mesh (45 micron) sieve. This fine gray powder is portland cement.

Brief Overview of Cement Chemistry[7]

During the burning operation in the manufacture of portland cement clinker, calcium oxide combines with the acidic components of the raw mix to form four principal compounds that make up 90% of cement by weight. Gypsum and other materials are also present. Following are the primary compounds, their chemical formulas, and abbreviations used by cement chemists:
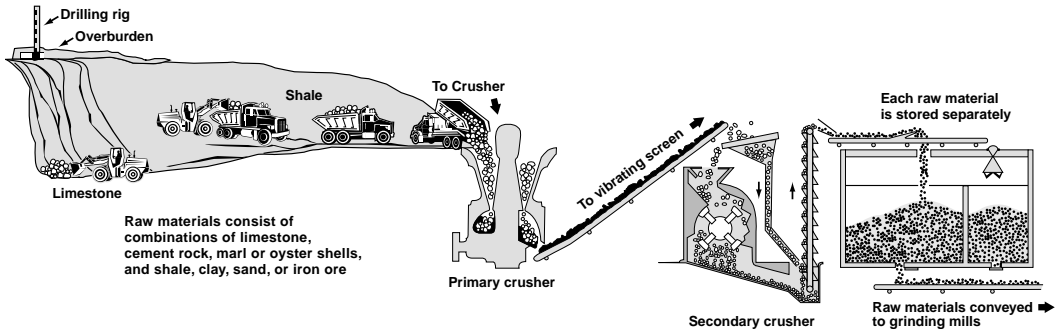
Tricalcium silicate	$3CaO \cdot SiO_2$	$= C_3S$
Dicalcium silicate	$2CaO \cdot SiO_2$	$= C_2S$
Tricalcium aluminate	$3CaO \cdot Al_2O_3$	$= C_3A$
Tetracalcium aluminoferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	$= C_4AF$

In the presence of water, these four compounds hydrate to form new ones that are the infrastructure of hardened cement paste in concrete. The calcium silicates, C_3S and C_2S, which constitute about 75% of the weight of cement, hydrate to form the compounds calcium hydroxide and calcium silicate hydrate (C-S-H) or tobermorite gel. The strength and other properties of hydrated cement are due primarily to the C-S-H. In the absence of sulfates, C_3A reacts with water to form calcium aluminate hydrates. C_4AF may also react with water to form calcium aluminoferrite hydrates. C_3A, gypsum, and water combine to form ettringite, a calcium sulfoaluminate hydrate. These basic compound transformations are as shown in Table A-1.
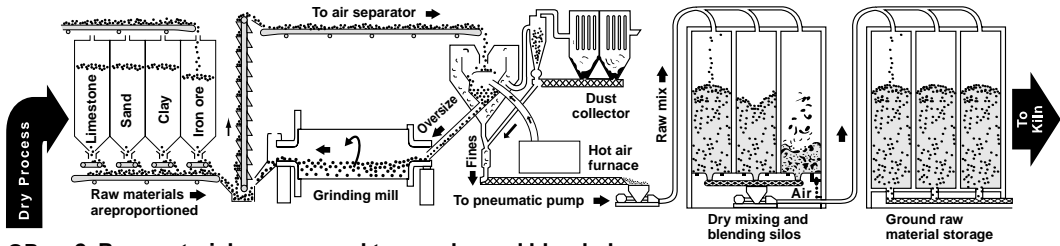
C_3S and C_2S in clinker and cement are also referred to as alite and belite, respectively. These and other compounds may be

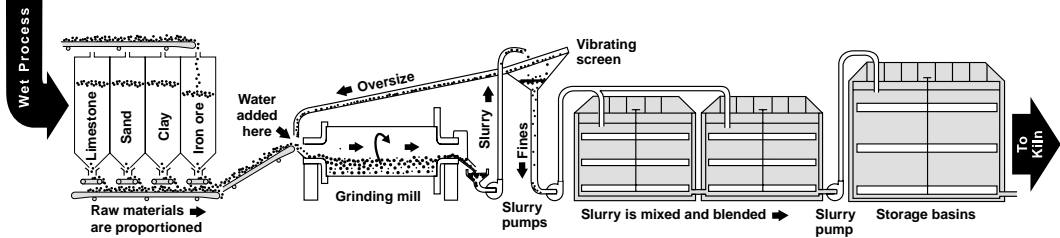---

[6] Adapted from Kosmatka and Panarese, 1988.
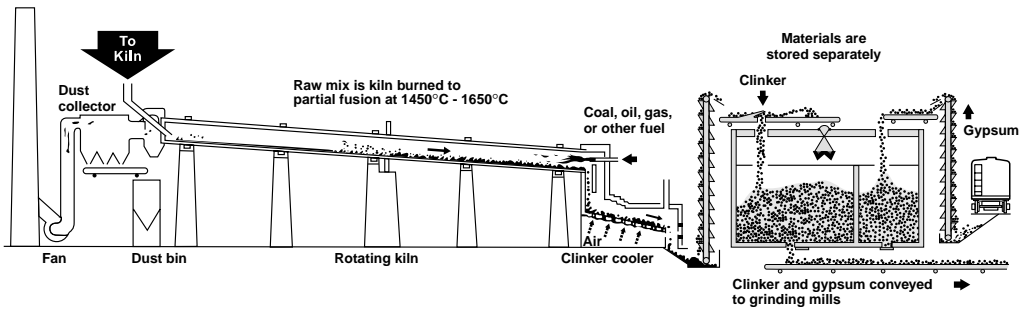[7] Adapted from Kosmatka and Panarese, 1988.

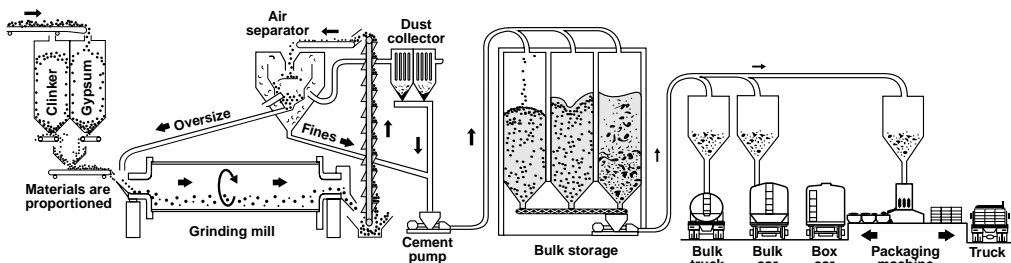**1. Stone is first reduced to 125 mm size, then to 20 mm, and stored.**

Dry Process

2. Raw materials are ground to powder and blended.

OR

Wet Process

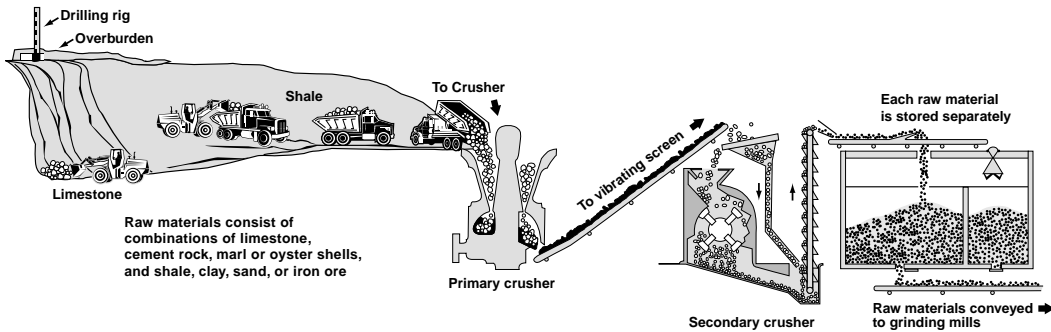**2. Raw materials are ground, mixed with water to form slurry, and blended.**

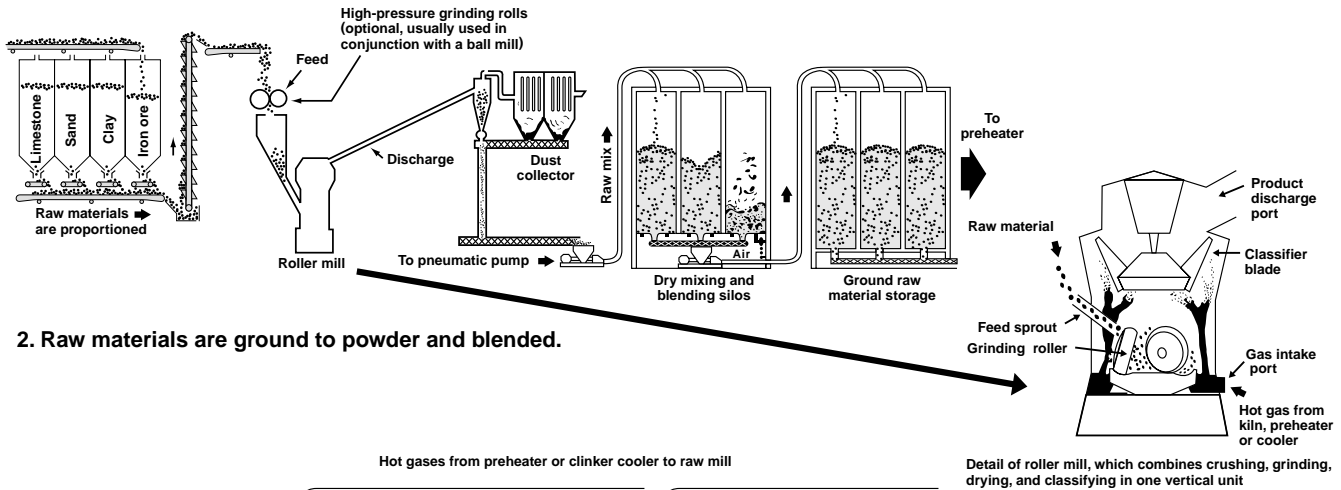**3. Burning changes raw mix chemically into cement clinker.**

4. Clinker with gypsum is ground into portland cement and shipped.
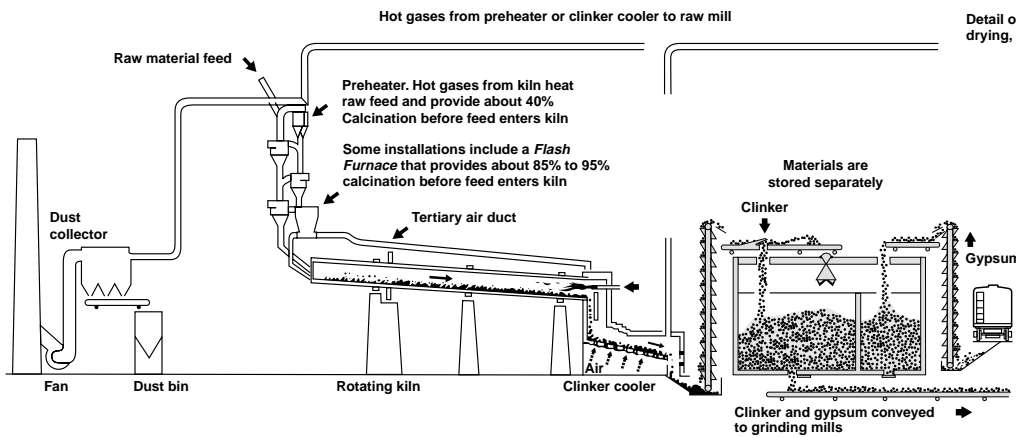
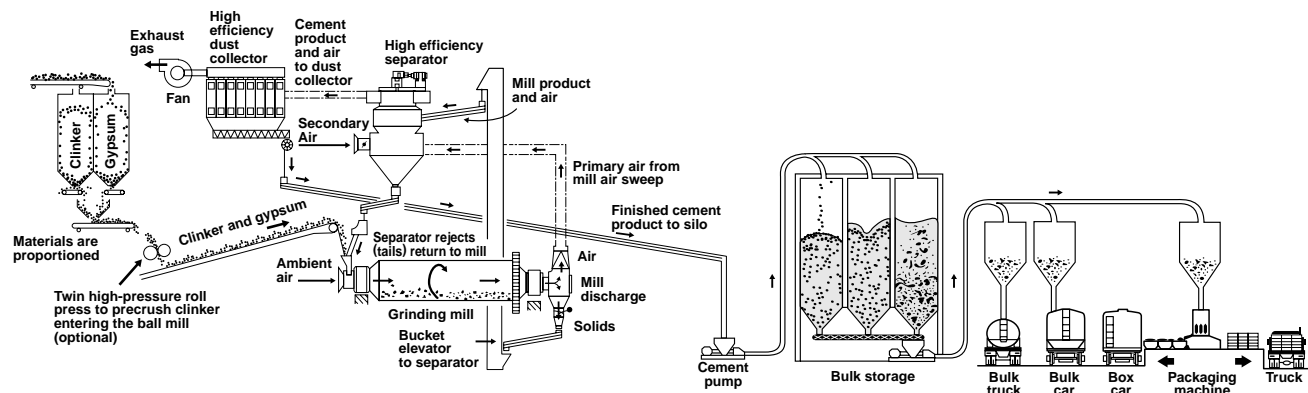*Fig. A-1. Steps in the traditional manufacture of Portland cement.*

1. Stone is first reduced to 125 mm size, then to 20 mm, and stored.

2. Raw materials are ground to powder and blended.

3. Burning changes raw mix chemically into cement clinker. Note four-stage preheater, flash furnaces, and shorter kiln.

4. Clinker with gypsum is ground into portland cement and shipped.

Fig. A-2. New technology in dry-process cement manufacture.

Table A-1. Portland Cement Compound Transformations

$2(3CaO \cdot SiO_2)$ (Tricalcium silicate)	+	$6H_2O$ (Water)	=	$3CaO \cdot 2SiO_2 \cdot 3H_2O$ (C-S-H)		+	$3Ca(OH)_2$ (Calcium hydroxide)
$2(2CaO \cdot SiO_2)$ (Dicalcium silicate)	+	$4H^2O$ (Water)	=	$3CaO \cdot 2SiO^2 \cdot 3H^2O$ (C-S-H)		+	$Ca(OH)_2$ (Calcium hydroxide)
$3CaO \cdot Al_2O_3$ (Tricalcium aluminate)	+	$12H_2O$ (Water)	+	$Ca(OH)_2$ (Calcium hydroxide)	=		$3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$ (Tetracalcium aluminate hydrate)
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (Tetracalcium aluminoferrite)	+	$10H_2O$ (Water)	+	$2Ca(OH)_2$ (Calcium hydroxide)	=		$6CaO \cdot Al_2O_3 \cdot Fe_2O_3 \cdot 12H_2O$ (Calcium aluminoferrite hydrate)
$3CaO \cdot Al_2O_3$ (Tricalcium aluminate)	+	$26H_2O$ (Water)	+	$3CaSO_4 \cdot 2H_2O$ (Gypsum)	=		$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ (Calcium trisulfoaluminate hydrate - ettringite)
$2(3CaO \cdot Al_2O_3)$ (Tricalcium aluminate)	+	$4 H_2O$ (Water)	+	$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ (Ettringite)	=		$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$ (Calcium monosulfoaluminate hydrate)

Note: Table A-1 illustrates only primary transformations and not the several minor transformations.

observed and analyzed through the use of microscopical techniques (see Figs. A-3 and A-4).

The approximate percentage of each compound can be calculated from a chemical analysis of the cement. X-ray diffraction techniques may be used to more accurately determine compound percentages. Tables A-2 and A-3 show typical compound composition and fineness for each of the principal types of portland cement for 1990s' and 1950s' materials, respectively.

Present knowledge of cement chemistry indicates that these compounds have the following properties:

Tricalcium silicate, C_3S, hydrates and hardens rapidly and is largely responsible for initial set and early strength. In general, the early strength of portland cement concrete is higher with increased percentages of C_3S.

Dicalcium silicate, C_2S, hydrates and hardens slowly and contributes largely to strength increase at ages beyond one week.

Tricalcium aluminate, C_3A, liberates a large amount of heat during the first few days of hydration and hardening. It also contributes to early strength development. Gypsum, which is added to cement during final grinding, slows down the initial hydration rate of C_3A. Without gypsum, a cement with C_3A present would set rapidly. Cements with low percentages of C_3A are especially resistant to soils and waters containing sulfates (external sulfate attack).

Tetracalcium aluminoferrite, C_4AF, reduces the clinkering temperature, thereby assisting in the manufacture of cement. It hydrates relatively slowly and contributes very little to strength. Most color effects are due to C_4AF and its hydrates.

Brief Overview of the Role of Sulfates in Hydration Reactions

The use of gypsum or other forms of calcium sulfate to control rapid stiffening in cement was discovered over a century ago [Hansen et al., 1988]. Gypsum, which is combined with cement
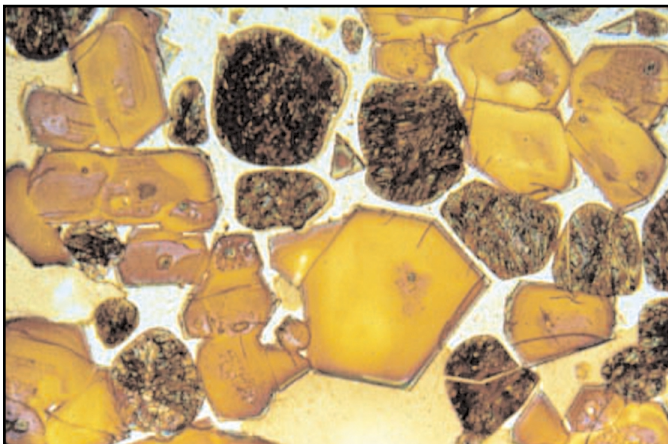

Fig. A-3 Polished thin-section examination shows alite (C_3S) as light, angular crystals. The darker, rounded crystals are belite (C_2S). Magnification 400X.

Fig. A-4 Scanning electron microscope micrograph of alite (C_3S) crystals. Magnification 3000X.

Table A-2. Chemical and Compound Composition and Fineness of 1990s' Cements*

Type of portland cement	Range of chemical composition, %						Loss on ignition, %	Na_2O eq	Range of potential compound composition, %				Blaine fineness, m^2/kg
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3			C_3S	C_2S	C_3A	C_4AF	
I (min-max)	18.7-22.0	4.7-6.3	1.6-4.4	60.6-66.3	0.7-4.2	1.8-4.6	0.6-2.9	0.11-1.20	40-63	9-31	6-14	5-13	300-421
I (mean)	**20.5**	**5.4**	**2.6**	**63.9**	**2.1**	**3.0**	**1.4**	**0.61**	**54**	**18**	**10**	**8**	**369**
II** (min-max)	20.0-23.2	3.4-5.5	2.4-4.8	60.2-65.9	0.6-4.8	2.1-4.0	0.0-3.1	0.05-1.12	37-68	6-32	2-8	7-15	318-480
II (mean)**	**21.2**	**4.6**	**3.5**	**63.8**	**2.1**	**2.7**	**1.2**	**0.51**	**55**	**19**	**6**	**11**	**377**
III (min-max)	18.6-22.2	2.8-6.3	1.3-4.9	60.6-65.9	0.6-4.6	2.5-4.6	0.1-2.3	0.14-1.20	46-71	4-27	0-13	4-14	390-644
III (mean)	**20.6**	**4.9**	**2.8**	**63.4**	**2.2**	**3.5**	**1.3**	**0.56**	**55**	**17**	**9**	**8**	**548**
IV (min-max)	21.5-22.8	3.5-5.3	3.7-5.9	62.0-63.4	1.0-3.8	1.7-2.5	0.9-1.4	0.29-0.42	37-49	27-36	3-4	11-18	319-362
IV (mean)	**22.2**	**4.6**	**5.0**	**62.5**	**1.9**	**2.2**	**1.2**	**0.36**	**42**	**32**	**4**	**15**	**340**
V (min-max)	20.3-23.4	2.4-5.5	3.2-6.1	61.8-66.3	0.6-4.6	1.8-3.6	0.4-1.7	0.24-0.76	43-70	11-31	0-5	10-19	275-430
V (mean)	**21.9**	**3.9**	**4.2**	**63.8**	**2.2**	**2.3**	**1.0**	**0.48**	**54**	**22**	**4**	**13**	**373**

 *Values represent a summary of combined statistics. Air-entraining cements are not included. Adapted from Gebhardt, 1995.

**Includes fine grind cements.

Table A-3. Chemical and Compound Composition and Fineness of 1950s' Cements*

Type of portland cement	Range of chemical composition, %						Loss on ignition, %	Na$_2$O eq	Range of potential compound composition, %				Blaine fineness, m^2/kg
	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	SO$_3$			C$_3$S	C$_2$S	C$_3$A	C$_4$AF	
I (min-max)	19.2-24.6	2.9-7.8	0.4-4.2	53.2-66.8	0.3-4.8	1.2-2.8	0.5-8.0	0.06-1.28	20-68	9-49	3-15	1-13	288-439
I (mean)	**21.4**	**5.7**	**2.7**	**63.9**	**2.3**	**1.9**	**1.3**	**0.53**	**51**	**23**	**10**	**8**	**332**
II (min-max)	21.0-24.5	4.0-5.9	2.6-5.2	61.1-65.0	0.3-4.7	1.3-2.3	0.4-2.4	0.14-0.73	39-50	24-39	4-8	8-16	298-406
II (mean)	**22.3**	**4.8**	**3.8**	**63.3**	**2.4**	**1.7**	**1.1**	**0.48**	**45**	**30**	**6**	**12**	**338**
III (min-max)	19.5-23.5	3.3-6.3	1.3-4.7	62.5-67.4	0.8-4.0	1.8-3.5	1.0-3.4	0.11-0.69	45-68	8-28	4-12	4-14	396-590
III (mean)	**20.9**	**5.0**	**3.0**	**64.5**	**2.0**	**2.3**	**1.8**	**0.40**	**59**	**16**	**8**	**9**	**477**
IV (min-max)	23.2-25.2	3.3-5.2	3.3-4.5	62.5-64.0	0.9-1.7	1.5-1.8	0.6-0.9	0.34-0.51	31-37	40-45	3-7	10-14	292-343
IV (mean)	**24.0**	**4.4**	**4.0**	**63.2**	**1.2**	**1.7**	**0.8**	**0.42**	**35**	**43**	**5**	**12**	**317**
V (min-max)	22.5-25.3	2.7-4.2	2.5-4.7	62.2-65.0	0.8-3.9	1.4-2.0	0.6-1.5	0.19-0.80	36-49	30-44	1-5	8-14	291-366
V (mean)	**24.1**	**3.5**	**3.5**	**63.9**	**1.9**	**1.6**	**1.0**	**0.38**	**44**	**36**	**3**	**11**	**327**

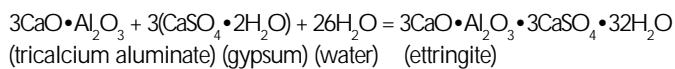*Air-entraining cements are not included. Adapted from Clifton and Mathey, 1971.

during finish grinding of clinker, is a mineral with the chemical composition $CaSO_4 \cdot 2H_2O$. Other forms of calcium sulfate are associated with dehydrated forms of gypsum. These forms occur naturally or as gypsum is heated to higher temperatures:

Gypsum ($CaSO_4 \cdot 2H_2O$)
- → Hemihydrate ($CaSO_4 \cdot {}^1/2H_2O$) at ~ 180 °C (350 °F)
  - → Soluble anhydrite ($CaSO_4$) at ~ 260 °C (500 °F)
    - → Anhydrite ($CaSO_4$) at ~ 650 °C (1200 °F)

The hemihydrate form is commonly called Plaster of Paris. Anhydrite is sometimes termed "hard burned anhydrite" and is less rapidly soluble than the other forms.

Although detailed discussion of the reaction chemistry is beyond the scope of this discussion, the basic reaction that occurs is that the gypsum combines with the tricalcium aluminate in the cement to form ettringite as follows:

$3CaO \cdot Al_2O_3 + 3(CaSO_4 \cdot 2H_2O) + 26H_2O = 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$
(tricalcium aluminate) (gypsum) (water)   (ettringite)

This reaction occurs very rapidly once cement comes into contact with mix water. Usually, the gypsum is consumed first and the remaining tricalcium aluminate (C_3A) will continue to react with the previously formed ettringite to create a compound called calcium monosulfoaluminate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$). Monosulfoaluminate takes up less space than ettringite. It is a stable compound unless additional sulfates become available whereby it can combine with these sulfates to reform ettringite in an expansive reaction. This is the basic mechanism for sulfate attack in hardened concrete subjected to external sulfate solutions.

Figure A-5 illustrates the formation of portland cement reaction products.

The work of Lerch serves as the foundation for our understanding of the role of sulfates in cement [Lerch, 1946]. Lerch showed that for a given cement chemistry there is an optimum level of
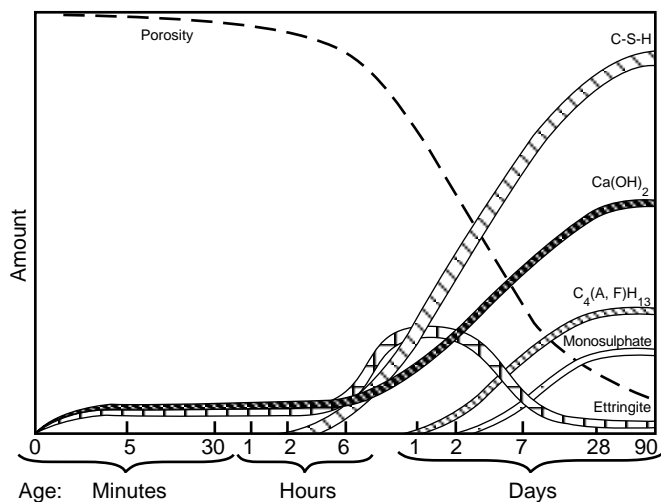

Fig. A-5 Schematic illustration of formation of reaction products and reduction of the volume of pore space with time in a portland cement paste. (Adapted from Locher, Richartz, and Sprung, 1976.)

gypsum to give best strength development and minimize shrinkage while avoiding rapid reactions that cause premature setting. The quantity of gypsum required increases with increasing C_3A content, alkali content, and fineness of cement. Thus, higher sulfate levels are associated with those characteristics of cement that increase early age (1 to 3 day) strengths. The optimum sulfate level generally increases for high-temperature curing, although cements are usually optimized under ambient temperature conditions.

Brief Overview of Changes in Cement Characteristics[8]

A survey of portland cements marketed in North America was conducted in 1994 under the sponsorship of the American Society for Testing and Materials (ASTM) Committee C-1 on Cement [Gebhardt, 1995]. The study reviewed 387 cements from 136 of 140 cement-producing facilities in the United States and Canada, plus several imported cements. The ASTM survey results can be compared with a study of cement characteristics done on 203 cements procured in 1953 and 1954 by the National Bureau of Standards (presently the National Institute of Standards and Technology) with the results published in 1965—1971 [Blaine, Arni and Foster, 1965; Clifton and Mathey, 1971]. In the 1950s' investigation, cement testing was performed by one of two laboratories. The ASTM survey contains information from reports or mill test certificates prepared by the cement manufacturer.[9]

For the most part, 1990s' cements are similar to 1950s' cements. However, changes have occurred over time, reflecting changes in raw materials, process requirements, and changes responding to construction needs. Table A-2 presents the chemical composition of the 1990s' cements; it includes the range of values (minimum to maximum) and the average (mean) value. Table A-3 illustrates similar data from the NBS study on cements from 1953 and 1954.

Modern cements generally gain strength more rapidly during early ages to meet the needs of current, more rapid, construction practices. This is illustrated in Figs. A-6 and A-7, which show changes in 1—28-day strengths. To meet higher early-strength requirements, C_3S content is slightly higher overall for most modern cements, anywhere from 3% to 10%. C_3S hydrates rapidly and is largely responsible for initial set and early strength (up to 7 days). Also, modern cements have increased fineness (surface area), which supports faster hydration and strength gain. Average alkali contents have shown some increases since the 1950s. For instance, the average alkali content of Type I is up 0.08%; alkalies also contribute to early strength development. The sulfate content for modern cements is about 0.5% to 1.2% higher than 1950s' cements, which is consistent with changes affecting early-age strengths. As was discussed earlier, there is a strong relationship between increases in the ratio of 1—28-day strengths and cement sulfate contents.

[8] See also "Portland Cement: Past and Present Characteristics," Concrete Technology Today, Portland Cement Association, PL962, July 1996.
[9] A more recent survey of mill test certificates, conducted by the Portland Cement Association in 1998, revealed essentially no changes from the 1994 ASTM results [Tennis, 1999].
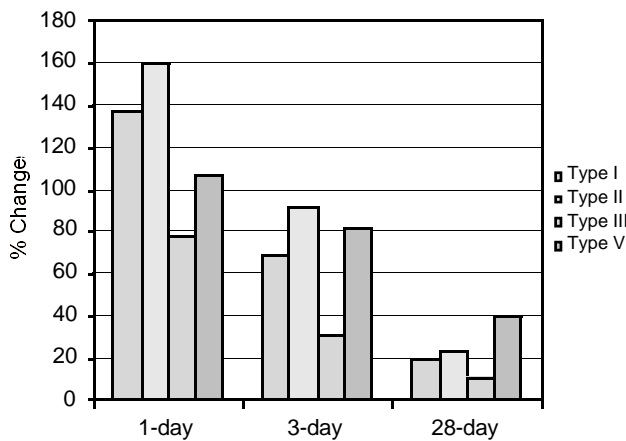
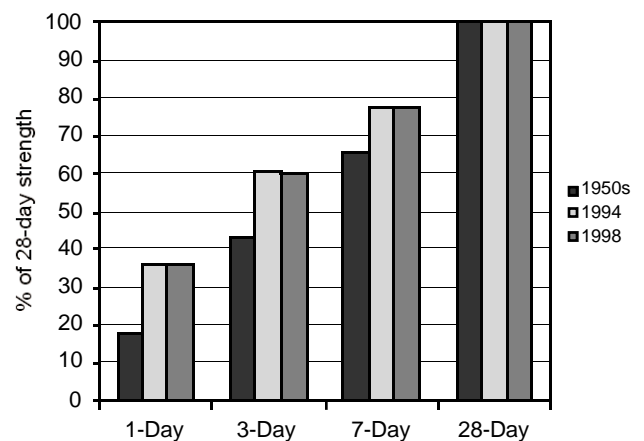**Fig. A-6 Changes in cement strengths from the 1950s to the 1990s.**

Fig. A-7 Changes in the ratio of early-age to 28-day strengths for Type I cements. The market has demanded higher early strength cements to meet today's construction requirements.

Modern cements gain strength more slowly than 1950s' cements beyond 7 days. Except for Type III, C_2S is from 5% to 14% lower for the modern cements. C_2S contributes largely to strength increase at ages beyond one week.

While cements have changed over the past 50 years, these changes are dwarfed by those that have occurred in concrete technology. The development and use of chemical and mineral admixtures have dramatically changed the design of concrete mixtures. Admixtures such as water reducers, retarders, fly ash, slag, and silica fume have given the designer a broad range of options for developing a concrete mixture for specific job requirements. In addition, new construction methods have impacted the mixing, transportation, placing, and curing of concrete. Thus, it is more important than ever to consider the entire concrete system in evaluation of performance.

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