

Reactions of Aggregates Involving Solubility, Oxidation, Sulfates, or Sulfides

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This report covers available information on reactions involving solubility or oxidation of aggregates while they are enclosed in concrete and reactions involving release of sulfates or sulfides from aggregates enclosed in concrete. Experience indicates that these phenomena may create local problems that usually take the form of unsightly conditions on concrete construction, such as staining or sporadic spalling and pop-out formation.

Reliable methods for detecting deleteriously reactive forms of ferrous sulfides in mineral aggregates would be a worthwhile addition to testing procedures in areas where these minerals have been found to be of significance in the performance of concrete.

•FOR MORE than two decades close attention justifiably has been given to research on reactions of aggregates involving alkalis and on methods by which potentially alkali-reactive aggregates or cement-aggregate combinations can be detected. However, chemical properties and reactions of aggregates not involving alkalis are locally of great significance, especially in architectural quality of concrete, and should be recognized in specifications and correlary methods of testing that serve as a basis for selection and control of aggregates and concrete.

This report is primarily a review of literature on reactions involving solubility or oxidation of aggregates while they are enclosed in concrete and reactions involving release of sulfates or sulfides from aggregates enclosed in concrete. Included also is information developed personally by the author and not heretofore reported, as well as certain data and information kindly made available to the author through personal communication by investigators now actively engaged in pertinent research. Notation of the latter type of information is made appropriately in the text.

Even a cursory review of experiences related to reactions of aggregates not involving alkalis shows that sulfates are the most significant and widespread substances that lie within the scope of this review. Moreover, they are significant in all of the individual categories of reactivity that are to be considered in this report. For example, many sulfate minerals are highly or moderately soluble in water and so must be considered in any review of the effect of solubility of aggregate constituents per se. Moreover, sulfates are commonly formed in aggregates as a result of oxidation of original sulfides, either before or after incorporation of the aggregate into concrete. Hence, they must be discussed in connection with both oxidation phenomena and the effect of sulfides. However, some sulfate minerals, such as alunite and jarosite, that may affect the performance of concrete are insoluble in water; and, moreover, the significance of the sulfates as constituents of aggregate is related to reactions in addition to their solubility. Therefore, sulfates occurring as primary constituents of aggregates are discussed also in a separate section of the report.

SOLUBILITY

Typical specifications and methods of test applied to aggregates proposed for use in concrete will cause rejection of aggregates whose structural soundness will be impaired by dissolution of its constituents while enclosed in concrete. However, natural aggregates, crushed stone, or aggregates composed of manufactured materials or industrial by-products may contain water-soluble or alkali-soluble substances that could react with the cement paste or produce efflorescence on surfaces of the concrete. Most important among such substances are alkali and alkali-earth sulfates. Specific effects of the sulfates are discussed later.

Sodium or calcium chloride sometimes is added to aggregates being transported during freezing weather to facilitate unloading operations. In such instances the concentration of chloride may be sufficiently high in portions of the concrete containing such aggregate to promote excessive corrosion of embedded steel or to produce unsightly and deleterious efflorescence.

Water-soluble materials in natural aggregates most commonly occur as coatings on the particles. Such coatings form at or near the ground water table in the deposit or, in arid areas, near the surface of the ground in the zone of soil moisture. A deposit may contain several zones of coated sand and gravel as a result of fluctuation of the position of the water table. Calcium carbonate or, in volcanic terrains opal, is the most common and predominant substance in coatings. However, locally, sulfates, chlorides, or phosphates are present. Gypsiferous coatings were found to be present on coarse aggregate produced from a deposit on the Boulder Canyon Project of the Bureau of Reclamation (1); because of the potentially deleterious effects on concrete, the allowable proportion of gypsum in the processed aggregate was restricted to 0.25 percent by weight of the coarse aggregate. By processing and washing of the aggregate the required results were obtained. Goldbeck (2) has reviewed the effects of surface coatings on aggregate, including the significance of soluble substances.

Water- or alkali-soluble minerals may be original constituents or they can be produced in almost any rock by weathering or other natural processes of alteration. Water-soluble alkali salts (particularly sodium carbonate) released from an altered granodiorite coarse aggregate are thought to have produced unsightly efflorescence and scaling of concrete on the downstream face of Florence Lake Dam in the southern Sierra Nevada in California (3). Apparently, zeolitic rocks and clay minerals of high cation exchange capacity can also release alkalis and other ions as a result of base exchange reactions while they are confined in portland cement concrete or mortar (5). Experience in England with efflorescence and scaling of concrete as a result of release of water-soluble substances by aggregate was described by Schaffer in 1932 (6). Peyton (7) has reported that weathering of sphalerite (ZnS) contained in chert aggregate in stockpiles produces zinc carbonate (smithsonite) which, upon dissolution in the alkaline media in concrete, causes excessive retardation of setting if present in more than minimal proportions. He concluded that the proportion of zinc carbonate in the aggregate should not exceed 0.30 percent by weight of the cement in the concrete. Gypsum is widespread in dolomite formations as scattered nodules and seams (Fig. 1).

Data published by the Bureau of Reclamation (8) show that the wide range of gravels, sands, and crushed rock tested, released between 0.000 and 0.710 percent of potassium (expressed as K_2O) and between 0.015 and 0.650 percent of sodium (expressed as Na_2O) during 28 days of treatment at 130 F in saturated lime water. The procedure for determining the proportion of alkalis released was developed originally in France by Rengade, et al. (9) as a part of an investigation of deterioration of concrete containing aluminous cements.

OXIDATION

Oxidation phenomena of significance to the performance of aggregates in concrete appear to be restricted to metallic iron and compounds containing ferrous iron. By far the greatest effect of oxidation in this context relates to the decomposition of the ferrous sulfides, pyrite (FeS_2), marcasite (FeS_2), and pyrrhotite ($Fe_{x-1}S_x$); that is, ferrous sulfides in which sulfur is stoichiometrically in excess of the iron.



Figure 1. Nodules of gypsum in stratified dolomite of the Lockport formation, near St. Catharines, Ontario.

Numerous reports, particularly by Knight (10-12) and by members of the staff of the Building Research Station in England (13), as well as others (14), describe deterioration of concrete containing altered dolerite (sometimes called Whinstone in the trade) that apparently results from expansion of the rock while contained in concrete as coarse aggregate. The deleterious effects are thought by several investigators to arise from partial oxidation of ferrous iron in secondary minerals, primarily chlorophaeite, a complex hydrous magnesium, iron, aluminum silicate. The chlorophaeite is an alteration product of olivine and pyroxenes. Many occurrences of alteration products of this type are now identified as the iron-bearing member of the montmorillonite group of clay minerals, namely, nontronite. The mechanism by which the oxidation might produce expansion or other deleterious effects has not been explained and no simple relation has been found to exist between the rate of oxygen uptake by the dolerite and its ability to cause distress of concrete (13). Studies of similar rocks in the United States have shown that adverse effects result from excessive volume change with wetting and drying because of the presence of nontronite. These studies are described by Rhoades and Mielenz (1). Similar conclusions were published recently by Milner (15). Oxidation is not thought to be involved in the volume change associated with the presence of nontronite.

Rhoades and Mielenz (1) and Swenson and Chaly (16) have reported adverse effects on concrete resulting from oxidation of ferrous compounds in clay ironstone concretions in the aggregate. The latter authors state: "Continued oxidation of iron compounds and hydration of iron oxide products in clay ironstones may cause pop-outs in concrete or extensive deterioration if present in large quantities." In general, these rock types should be detectable by standard physical tests of aggregate for concrete, and they are readily identified by petrographic examination.

Metallic iron occurring in aggregate is susceptible to oxidation and to hydration of the resulting oxides if the particles are exposed at the surface of the concrete. Metallic iron occurs as nodules and blebs in blast-furnace slag, and Seaton (17) reports the presence of metallic iron in cinder aggregates as a result of complete reduction of original ferric and ferrous iron during the combustion of coal or coke. In addition, metallic iron is employed as aggregate in some proprietary admixtures, grouts, and mortars to increase strength and abrasion resistance and to control shrinkage. In

properly proportioned, compacted, and cured concrete and mortar, the effects of oxidation of metallic iron are superficial and not progressive, resulting only in minor pitting and staining of surfaces (18, 19).

The effects of oxidation of the ferrous sulfides in aggregate have been studied most definitively by Midgley (20), Hagerman and Roosaar (21), Moum and Rosenqvist (22), and Seaton (17). Ingham (23) is carrying forward comprehensive studies of reactions of sulfides in aggregates being used in Ontario. Midgley and Seaton confined their studies to pyrite, whereas the Norwegian investigators investigated both pyrite and pyrrhotite. Rhoades and Mielenz (24) noted the conflicting experience with reactivity of pyrite in concrete and reported the successful use of highly pyritiferous aggregates from the vicinity of Cripple Creek, Colorado. Extensive studies by Midgley (20) of pyrite in chert aggregates of the Thames River reveal that pyrite can be classified into reactive and non-reactive types. The two types are distinguished by the absence or presence in the crystallographic structure of trace amounts of various metallic elements other than iron. These miscellaneous elements stabilize the structure and render the mineral less susceptible to oxidation in an alkaline environment. Hagerman and Roosaar (21) showed that pyrrhotite is commonly very susceptible to rapid alteration while enclosed in concrete and that maximum effects are produced by mixtures of pyrrhotite and pyrite. These findings are consistent with the observations of Ingham (23), who noted that pyrite and marcasite are caused to undergo rapid oxidation reactions adjacent to inclusions of lead sulfide (galena) or copper-iron sulfide (chalcopyrite). He found that pyrite in high-temperature veins was not subject to oxidation, whereas pyrite, marcasite, and pyrrhotite in low-temperature hydrothermal veins are subject to rapid oxidation in the presence of an electrolyte.

Oxidation of pyrite, marcasite, or pyrrhotite in the presence of hydroxyl ion in excess of the normal concentration in water causes the formation of ferrous sulfate, ferric hydroxide, and sulfuric acid as a preliminary step, followed by hydrolysis of the ferrous sulfate to ferric hydroxide and sulfuric acid. Interaction of the sulfuric acid with calcium hydroxide produces calcium sulfate, which in turn produces calcium sulfoaluminate by interaction with aluminates in the cement paste. The resulting substantial increase in solid volume in the system causes expansion with accompanying cracking and pop-out formation on the concrete. Reports of experiences in the United States indicate that these effects usually are limited to production of unsightly conditions, rather than to general deterioration of the concrete. Field experiences with pyritiferous aggregates in the United States are described by Litehiser (25), Rhoades and Mielenz (1, 24), Mielenz (26, 27), Seaton (17), and others (Figs. 2 and 3).

Three procedures are available for detection of potentially deleterious types and proportions of ferrous sulfides; namely, (1) a qualitative chemical test described by Midgley (20), (2) a semi-quantitative chemical test described by Seaton (17), and (3) a quantitative test of concrete beams described by Hagerman and Roosaar (21). The Midgley procedure is very rapid, involving the immersion of suspected particles in saturated lime water and observation for the formation of blue-green ferrous sulfides that turn brown on exposure to air. The reactions are completed within 30 min. According to Midgley, lack of such reactions in 30 min indicates that the ferrous sulfides are absent or are not potentially deleteriously reactive in concrete. The present author has applied this test to numerous samples of pyritiferous dolomites, limestones, diabases, and metamorphic rocks; none proved to be reactive by these criteria. However, pyrite in a shale particle taken from an iron-oxide stained pop-out in concrete proved to be reactive. Ingham (23) found pyrite, marcasite, chalcopyrite, and pyrrhotite in samples of vein quartz, shale, fluorite vein deposits, sphalerite ore, chlorite schist, magnetite skarn, limestone, and dolomite to be non-reactive, whereas pyrite in samples of a rhyolite, another quartz vein deposit, and hydrothermal vein material in magnetite skarn proved to be reactive in the Midgley test.

The Seaton procedure is now incorporated in ASTM Specifications C 330 and C 331 on lightweight aggregate (28). The method involves exposure of a portion of the aggregate in a steam bath for 16 hours, after which the degree of stain resulting from the liberation of iron compounds is noted and the proportion of such compounds is determined by partial chemical analysis.

In the test described by Hagerman and Roosaar (21), the aggregate is incorporated in concrete beams fitted with terminal gage studs and the specimens are subjected to laboratory or outside storage for periods up to several months, during which time the dynamic modulus of elasticity and length change are determined. Beams in which the aggregate contained 14 percent of pyrrhotite expanded about 0.6 percent in outside exposure during a period of $2\frac{1}{2}$ months.

Oxidation of calcium sulfide in blast-furnace slag aggregates while they are enclosed in concrete has been a subject of concern (13, 29). The possible oxidation of calcium sulfide in slags before their incorporation in concrete is discussed below. According to Josephson, Sillers, and Runner (29), the sulfur content of American blast-furnace slags ranges from about 1 to about 3 percent by weight. The sulfur is present in the slag as microscopically crystalline calcium sulfide, less commonly as ferrous or manganous sulfides, or dissolved or dispersed colloiddally in the interstitial glass. In view of the solubility of calcium sulfide in alkaline solutions, fears have been expressed that the sulfide sulfur would be subject to progressive oxidation in the concrete, with production of free sulfate ion that would be capable of converting aluminates to calcium sulfoaluminate and thus cause deleterious expansion of the cement paste. However, no reports of adverse effects of this type occurring in the United States were found in the literature.



Figure 2. Surface of concrete retaining wall displaying staining and surface pitting produced by oxidation and hydration of pyrite in a particle of coarse aggregate. Magnification $\times \frac{1}{4}$. (Courtesy of the Ohio Department of Highways.)

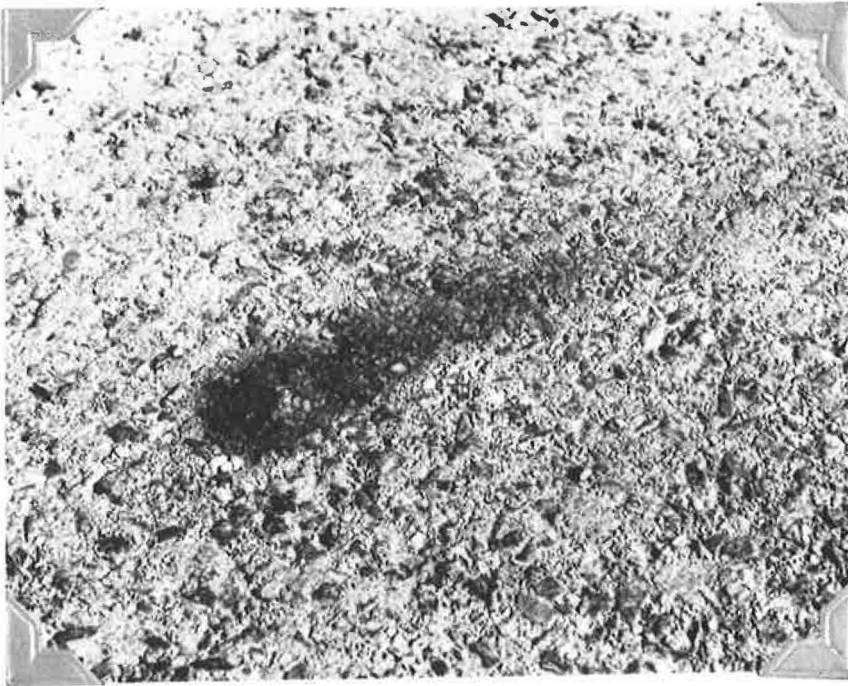


Figure 3. Iron oxide staining of bituminous concrete pavement as a result of oxidation and hydration of pyrite and marcasite in diabase coarse aggregate. (Courtesy of the Ontario Department of Highways.)

In 1955, R. H. Bogue (30) stated:

Before slags could be generally accepted as a satisfactory material for use, either as admixture in cement or as aggregate in concrete, it was necessary to establish that none of their constituents compounds would react detrimentally with the paste. Of these compounds, the sulfide sulfur has sometimes been held in distrust on the basis that it might undergo oxidation and cause expansion of the concrete or corrosion of the reinforcement. This view has been shown, by a half century of successful use, to be groundless.

Nevertheless, this matter is viewed with continuing concern in England, with the result that the Building Research Station and the British Slag Federation are at this moment engaged in re-examination of this question (31). ASTM (28) and Federal Specifications on blast-furnace slag aggregate include no limitations on sulfide or sulfate sulfur, a consequence of the lack of adverse experience in the United States. On the other hand, British Standard No. 1047 on air-cooled blast-furnace slag aggregate for portland cement concrete limits the acid-soluble sulfate of coarse aggregate to a maximum of 0.7 percent, expressed as SO_3 , and the total sulfur to 2 percent (13). No limits on sulfate or total sulfur are placed on blast-furnace slag fine aggregate.

Most of the experimental work concerned with the effect of sulfide and sulfate sulfur in blast-furnace slag aggregate upon the durability of concrete was carried out many years ago in Germany by Grun and others and is summarized by Keil (32) and by Lea (13). Work on this subject conducted in England during 1936-40 was summarized in 1950 by Parker (33) and later concepts were published by him in 1961 (34). The later report presents data on slag aggregate selected in commercial gradation from seven sources. All of the slags had favorable service records although some had been

employed as aggregate only in bituminous concrete. Total sulfur was found to range from 1.20 to 2.25 percent in the fine aggregate and from 1.05 to 2.29 percent in the coarse aggregates. Sulfate sulfur (as SO_3) was found to range from 0.07 to 0.70 percent in the fine aggregates and from 0.09 to 0.69 percent in the coarse aggregates.

Parker prepared concrete specimens proportioned 1:2:4 (cement: fine aggregate: coarse aggregate) and observed change of length over extended periods under several conditions of storage. Specimens stored in air or in water in the laboratory for two years showed no adverse effects. Also, over the course of 33 months, specimens containing aggregates from each of five of the sources showed no abnormal action during exposure to natural weathering. However, specimens containing either of two of the aggregates expanded progressively during natural exposure and in ten months the expansion attained 0.084 and 1.24 percent linearly in the two sets of specimens. Chemical analysis of the expanded specimens showed that a considerable proportion of the sulfide sulfur had oxidized to sulfate during the period of exposure. On the other hand, a minor degree of oxidation was found to have occurred in the specimens that did not expand significantly.

The data show that the total sulfur content did not determine the extent of expansion nor did the expansion correlate with the proportion of sulfide sulfur that had been oxidized to sulfate before the slag was incorporated into the concrete. Parker concluded tentatively that the extensive oxidation of the sulfide sulfur in the affected slags while they were enclosed in concrete related to simultaneous occurrence of three phenomena; namely, (1) presence of an unusually high proportion of crystalline calcium sulfide, (2) high porosity of the slag, and (3) susceptibility of the concrete containing those particular gradings of coarse and fine aggregate to cracking during exposure to weathering. That is, he believed the degree of oxidation to be related to a basic susceptibility of the slag and accessibility of the interior of the concrete to air and moisture. The sound slags were pit or bank slags, whereas the two unsound slags were coarse-grained, so-called ball-cooled slags, that is, slags that were allowed to solidify in the ladle.

It must be emphasized that one of the slags producing the large expansion of concrete specimens is widely and successfully used in precast portland cement concrete units in exposed situations. No evidence of unsoundness has been observed in practice. The other apparently unsound slag is used only in bituminous concrete.

Parker recommended limitation of permissible total sulfur content to 2 percent, use of natural sand as fine aggregate in combination with blast-furnace slag coarse aggregate, and restriction of blast-furnace slag for use in portland cement concrete to rapidly cooled, very finely crystalline types so as to minimize the proportion of well-crystallized calcium sulfide.

In the United States, the bulk of the slag used for production of concrete aggregate is air-cooled in pits or banks (35). The remainder is specially processed to produce granulated or expanded blast-furnace slags. According to Lewis (36), so-called ball-cooled slag is not used in production of concrete aggregate in the United States. Moreover, ball-cooling of slag is decreasing in England because the ladles are not thereby used efficiently, and difficulty is experienced in processing of the extremely large masses of slag.

Calcium sulfide in blast-furnace slag aggregate is released into the alkaline solutions pervading portland cement paste in concrete so that sulfide ions are available for interaction with iron-bearing phases of the cement. Particles of blast-furnace slag aggregate typically are surrounded by a zone of blue-green or green stain in the cement paste (Fig. 4), and commonly the stain permeates the entire matrix. The color fades with drying of the concrete and penetration of oxygen into the outer part of the concrete so that the cement paste adjacent to exposed surfaces usually is pale buff in color. If drying is prevented, the greenish coloration of the cement paste extends to the surfaces, sometimes producing a mottled appearance on the concrete. Viewed at high magnification, the stained cement paste is seen to include minute green masses that are dispersed through the hydration products of the cement. Similar features are observed in the paste of portland blast-furnace slag cement. Sulfides can also penetrate into concrete from base-course aggregate composed of blast-furnace slag.

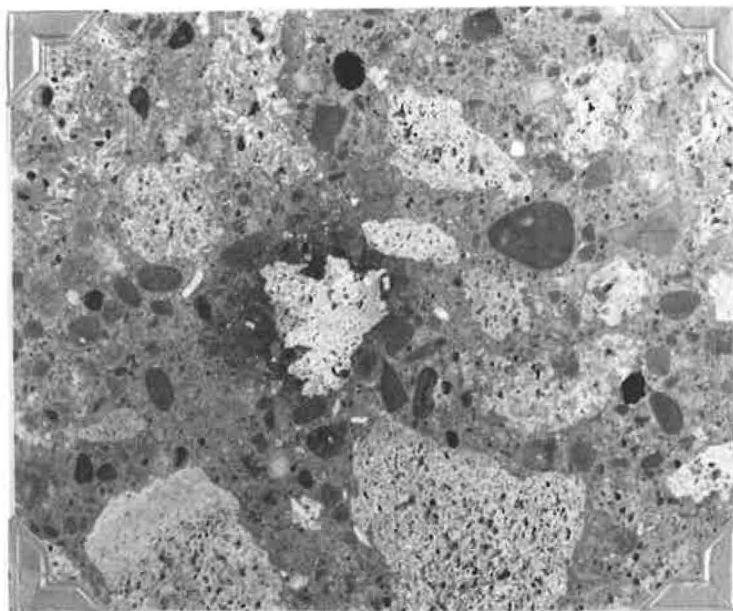


Figure 4. Dark green stain in cement paste surrounding a particle of air-cooled blast-furnace slag in coarse aggregate (natural size).

Examination of many samples of concrete characterized by such staining has revealed no evidence that the chemical reactions or the physical effects resulting therefrom are harmful. A similar conclusion was reached by Mather (37) following detailed study of concretes containing portland blast-furnace slag cements.

State of Ohio Department of Highways specifications on fine aggregate for portland cement concrete (38) include a limitation on the maximum permissible content of sulfide sulfur (namely, 0.3 percent as sulfur) as determined in accordance with ASTM Method C 25. The specification is not a basis for rejection of the aggregate but is to indicate whether the aggregate requires further investigation before acceptance. Presumably, the limitation is a method for controlling the proportion of pyrite that may be present in the fine aggregate.

SULFATES

As has been mentioned repeatedly, sulfates may be present in aggregate of diverse types, either originally or as a result of oxidation of original sulfides. In each instance the sulfates are important mainly because they may promote attack upon the aluminates or calcium hydroxide in the cement paste, with consequent expansion, cracking, and general deterioration of the concrete. The following discussion considers only those aggregates that include water- or alkali-soluble sulfate at the time they are incorporated into the concrete.

Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is the most common of the water-soluble sulfates that occurs in aggregate materials. It occurs as coatings on natural gravel and sand; it occurs as a natural component of various rocks, such as dolomites (Fig. 1); it is a common product of natural weathering or other alteration, such as natural oxidation of sulfides; and it is formed in blast-furnace slags as a result of weathering in the pits and stockpiles. In addition, anhydrite (CaSO_4) may occur in cinders or other calcined natural materials as result of dehydration of gypsum (17); the anhydrite may hydrate to gypsum before or after incorporation of the aggregate into concrete. According to

Seaton (17), the resulting volume change can create distress of concrete if the particle is enclosed in hardened cement paste.

Additional information is required to establish the rate and the conditions under which water-soluble sulfate is formed during natural exposure of air-cooled and granulated blast-furnace slag. The problems associated with this determination are formidable and must be approached with caution if reliable data are to be obtained. Microscopical study of blast-furnace slag aggregates indicates that the sulfates occur in several forms. Well-developed crystals of gypsum sometimes are readily observed in voids in weathered particles (Fig. 5), and very finely divided gypsum may occur in superficial coatings on particles in slag that has been exposed for prolonged periods. In addition, a portion of the sulfate may react with the interstitial glass phase of either air-cooled or granulated blast-furnace slag, resulting in formation of calcium sulfoaluminates that occurs as fibrous linings on voids in the slag. Also, the sulfide sulfur occluded in the glass phase may become oxidized without necessarily being available for release into the cement paste of concrete. Consequently, the mere analytical determination of total sulfate in a slag aggregate or the determination of the increase in sulfate content of a slag that is contained in concrete is not a measure of the deleterious effects to be expected.

It is also to be recognized that the analytical procedures necessary for accurate determination of sulfate in a blast-furnace slag must be carried out with utmost care so as to avoid oxidation of the sulfide sulfur during the determination itself. The procedures should establish quantitatively the presence of sulfate already bound as calcium sulfoaluminates in contrast to the sulfate that exists in forms that are potentially available for deleterious interaction with constituents of the cement paste.

Lea (13) discusses the effects of sulfate in aggregates produced by crushing of brick. Although this type of aggregate is of little concern in the United States, the experience with this material is of value as a means to evaluate the tolerable proportion of sulfate in aggregate for use in portland cement concrete. These studies indicate that sulfate content as high as 1 percent (as SO₃) can be tolerated even in very lean concrete mixtures.

Laboratory tests show the complex potassium aluminum sulfate, alunite, to be highly reactive with portland cement paste (39, 40). Jarosite, the iron-bearing equivalent

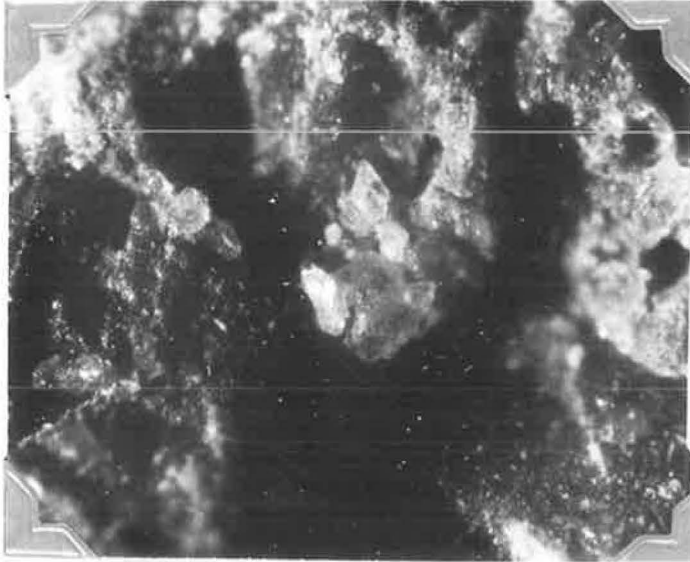


Figure 5. Gypsum crystals in weathered particle of air-cooled blast-furnace slag (magnification $\times 50$).

of alunite, is expected to react similarly. Alunite is of very restricted occurrence, but jarosite is common as a minor constituent of shales, phyllites, schists and other micaceous rocks, the jarosite having formed by interaction of the products of decomposition of ferrous sulfides, primarily pyrite, with mica and hydromicas.

CONCLUSIONS

Reactions of aggregates involving solubility, oxidation, sulfates, or sulfides are indicated by published information and the experience of the author to be of minor significance generally. Aggregates containing sulfides or sulfates may create local problems that are primarily the development of unsightly conditions on concrete construction, such as efflorescence, staining, or sporadic spalling and pop-out formation.

At this time, it appears that reliable methods of testing for detection of reactive forms of ferrous sulfides in mineral aggregates would be a worthwhile addition to testing procedures in localities where these minerals have been shown to be of significance in the performance of concrete.

Petrographic examination should be of value in identification of aggregates suspected of susceptibility to solubility, oxidation, or reactions of sulfides or sulfates while enclosed in concrete.

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