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Contents

Anhydrous Minerals and Organic Materials as Sources of Distress in Concrete

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• THE PURPOSE of this report is to define the extent of the problems that exist with respect to the deterioration of concrete from reactions involving (a) hydration of partially or completely dehydrated components of the aggregate, and (b) reactions of organic materials associated with aggregates. The first part of this assignment is to theorize as to what compounds could exist in either natural or artificial aggregates in forms in which they might cause distress in concrete by combining with water. This approach applies also to what might be classed by-product aggregates such as cinders and slags.

OXIDES

Certain oxides, such as calcium and magnesium, can react with water to form hydrated oxides or hydroxides. The latter occurs in nature as periclase, primarily in metamorphic silica-poor dolomitic limestones and dolomites, where dolomite has been decomposed to calcite and MgO near igneous contacts. However, there appear to be no recorded instances of distress in concrete produced by natural periclase. Calcium oxide probably never occurs in nature and accordingly would never be found in natural aggregates except as a contaminant. Contamination with calcium and magnesium oxides has occurred where railroad cars and trucks have been used to transport either quicklime or a refractory material, known as deadburned dolomite, immediately prior to the transport of aggregates.

Also, lightweight aggregates are produced by expanding shales and clays at temperatures at which calcite and dolomite are converted to oxides. Hence, if the raw materials contain either or both of these carbonate minerals, calcium or magnesium oxides or both would be present in the aggregate as discharged from the expanding kiln. However, these oxides may or may not cause harmful expansions in concrete because as is well known, the rates at which these oxides react with water depend on the temperature and time of calcining. That is, what is classed as soft-burned lime, hydrates almost immediately on contact with water, whereas a hard-burned lime reacts slowly with water. If the lime or magnesia in the aggregate reacts with the water before the paste sets, it will not cause expansion of the concrete. On the other hand, if one or both continue to hydrate for days or months, they can produce harmful expansions. This will be true of any reactive material. That is, to produce harmful expansion the reaction with water must be one that is not completed within a very short time, possibly a few hours, after the aggregate has come in contact with water.

Nordberg (1) in describing a lightweight aggregate plant made the following statement: "Shale is trucked to the plant, crushed through hammermills, screened into four sizes and fed into separate kilns and calcined at 1900 F. An innovation is the slaking of the calcined shale for the removal of free lime." From this statement, it appears that calcium and magnesium oxides are uncommon in this type of aggregate but that in at least one plant the aggregate did contain free lime as discharged from the kiln.

While on the subject of expanded clays and shales, it seems desirable to point out that gypsum, $CaSO_4 \cdot 2H_2O$, might be a source of trouble if the raw materials were contaminated with it. This mineral could be dehydrated during the expansion process

to a form of anhydrite that would hydrate slowly in concrete. The writer is not aware of any such experience with gypsum in this type of aggregate, but it should be recognized as a possible source of trouble.

Iron blast-furnace slag is a common aggregate which is produced by reacting flux stone with the gangue of iron ores in blast furnaces. The flux stone usually is mostly calcium carbonate containing a few percent of magnesium carbonate with very minor amounts of other materials such as silica. In the normal operation of a blast furnace, the flux stone and gangue are completely combined in the form of a molten glass as discharged from the furnace. However, Josephson, Sillers and Runner (2), in discussing deleterious materials in blast-furnace slag as used as an aggregate in concrete, state: "In more than 30,000,000 cubic yards of concrete containing slag aggregate used in the past forty years, about thirty known instances of spalls or pop-outs have been caused by swelling of extraneous materials delivered in the slag. The cause and prevention of pop-outs were thoroughly investigated by M. A. Muskopf . . . . Contrary to the belief of blast-furnace experts, he found that incompletely fused fragments of flux stone could be discharged along with slag under certain rare conditions and were quite harmless in concrete if slaked before the concrete set, but that, if of a particular composition approaching a deadburned magnesite, they could hydrate so slowly as to slake and produce spalls or pop-outs after the concrete had set. "

The authors go on to point out that such fragments can be rendered harmless by simply spraying the slag, in the pit, with water while still hot. These findings are now well known and commercial-slag producers reject doubtful slag and regularly wet all of their slag while it is hot. It appears, therefore, that there is not much danger from harmful reactions in concrete from the hydration of calcium and magnesium oxides in blast-furnace slag aggregates.

Holt (3) reported on the examination of 400 samples of concrete made to determine the cause of unsatisfactory performance. He found one aggregate that contained uncombined calcium oxide.

Swenson and Chaly (4) point out that minerals such as pyrite and marcasite may first be oxidized and then hydrated to sulfuric acid and iron oxides with large increase in volume. Also that continued oxidation of iron compounds and hydration of iron oxide products in clay ironstones may cause pop-outs in concrete and extensive deterioration if present in large quantities. Midgley (5) reported on staining of concrete by pyrite.

ZEOLITES

Bredsdorff, et al. (6) point out that zeolitic minerals and some clays of the montmorillonite type are subject to base exchange by which calcium ions from cement paste are exchanged for sodium and potassium ions in these materials. They suggested that this could influence alkali-aggregate reactions. These materials have also been suspected of causing expansion in concrete.

Zeolites are secondary minerals formed by the hydration of alkali and alkaline earth aluminum silicates. According to Hey (7), W. L. Bragg pointed out that silicates are, in general, built up of cations of the stronger bases, together with anions composed of silicon and oxygen, or silicon, aluminum, oxygen, and hydroxyl groups or water molecules. The anion is a non-polar bonded structure in which silicon (or aluminum) and oxygen alternate, and may be small finite groups, or may be infinitely extended into one, two or three dimensions (strings, sheets, or blocks).

The last case, blocks, is characterized by the ratio of $(Al + Si) = 2$. It is exemplified by the various forms of silica; but cations cannot enter into such a structure unless aluminum or other trivalent atoms replace part of the silicon when cations enter to balance the electrovalence. W. H. Taylor has shown that analcime, a zeolite, does exemplify this structure. It consists of an infinite tridimensional anion in which silicon or aluminum and oxygen alternate, forming an open framework within which sodium ions and water molecules are arranged. The meshes of the anion framework are large enough to permit passage of the water molecules and sodium ions, thus allowing dehydration and base exchange, whereas the strong non-polar bonds of framework permit these reactions to take place without destruction of the structure.

The open structure of the anion permits the removal of water from the crystal and the stability of the ions permits this without disturbance of the structure. If the dehydration is carried out at low temperature in a vacuum, the lattice does not shrink and the rehydration is rapid. If the dehydration is carried out at higher temperatures and for prolonged periods, there is a tendency for the lattice to shrink and then the reabsorption of water is prevented or at least reduced to a slow rate.

The zeolites have the property of being able to exchange cations when immersed in a solution of a salt for the cations of that solution, base exchange. This exchange is controlled by the valence of the cations; i. e. , one calcium ion will replace two sodium ions. This exchange takes place without any change in the structure of the anion. This ability of the zeolites to lose and regain water and to exchange cations without change in the volume of the unit cell of the crystal should, it seems, render them harmless from the standpoint of producing expansions in concrete. However, there are two zeolites that behave differently from the others. The zeolite laumontite on exposure to air or to gentle heat loses about one-eighth of its water to form leonhardite. This occurs with a change in the volume of the unit cell of about 1. 5 percent. Sometimes this occurs with the crystal changing to a powder. The reaction is reversible and fairly rapid. According to Coombs (8) the rehydration may be as brief as 1 or 2 hours. It appears from this that this rehydration process might be sufficiently slow to produce a volume change in concrete that would result in harmful expansion if leonhardite was a component of an aggregate. Pearson and Loughlin (9) believed that this hydration caused disintegration of cast stone and stucco in an area where leonhardite occurred as a constituent of weathered anorthite.

According to Kaley and Hanson (10), zeolites may occur in sedimentary rocks as well as in rocks of igneous origin. This occurrence of a zeolite was in a feldspathic sandstone from a depth of about 11,000 feet in an oil well.

CLAYS

Clays are a class of minerals that are believed, under certain circumstances, to be harmful in concrete. Holt (3) concluded that 44 of the 400 samples of concrete examined in his studies of complaints contained excess clay or loam. However, in these cases there probably were no expansive reactions involved because of reaction of any clay mineral with water in the hardened concrete. These are probably simply cases in which the clay and loam interfered with the bonding of the hardened cement paste to the aggregate and resulted in low strengths.

According to Grim (11), there are three general structural types among the clay minerals: layer structures of two types and one fibrous structure. One of the layer types is composed of unit layers, with each layer consisting of one silica tetrahedral sheet and one octahedral sheet tied together in a common sheet with shared oxygens. The units are stacked one above the other in the c-axis direction. Kaolinite is an example of this type of structure, and in well-crystallized kaolinite there is a regular stacking arrangement of silicate units. Halloysite has a similar structure, but successive silicate layers are shifted in a more or less random fashion, in both horizontal directions (the a- and b-axis directions), and a layer of water a single molecule thick may separate the silicate layers. Further, the layers may be curled or rolled up into tubes. Still other clay minerals of this type are intermediate between kaolinite and halloysite in that they show random stacking with shifts in only the b-axis. Such material is generaly designated poorly oriented kaolinite.

The other layer structural type is composed of two silica tetrahedral sheets with a central octahedral unit held together by two common sheets, with shared oxygens. The layers are stacked one above the other in the c-axis direction. In this type of structure there may be substantial substitutions of aluminum for silicon in tetrahedral positions and the populations of the octahedral positions may be either aluminum, iron, or magnesium, alone or in combination. Illite and chlorite belong in this structural category.

Montmorillonite, another member of the second structural category, has substitutions largely in the octahedral positions which are balanced by a variety of interlayer cations which are loosely held and which are exchangeable. Successive silicate layers

are loosely held together, and layers of water or other polar molecules of variable thickness may enter between the silicate layers, separating them. The thickness of the interlayer zone varies with the nature of the interlayer cation and the amount of available water or other polar molecules. Montmorillonite, unlike illite or chlorite, in which the interlayer cations tie successive sheets together firmly, has an expanding lattice with a variable c-axis.

Vermiculite, still another member of the second structural category, is similar to both chlorite and montmorillonite. The unbalancing substitutions are largely in the tetrahedral part of the structure, and the interlayer balancing cation is largely magnesium, which, however, is hydrated rather than encased in hydroxyls in octahedral coordination. As indicated, interlayer water is present, and the mineral expands. The amount of interlayer water or other polar material is variable. In vermiculite, unlike montmorillonite, the expansion is limited.

Attapulgite is representative of the fibrous type of clay minerals. It is composed of ribbonlike layers of two silica tetrahedral units tied together by a central octahedral unit, through common oxygens. The ribbons are tied together at their long edges, through common oxygens, to provide a gutter-and-channel type structure. Much remains to be learned about this type of clay mineral.

It seems evident from this review of the structures of the clay minerals that clay minerals of the first structural category such as kaolinite, and those of the third structural category, such as attapulgite, will not undergo volume change in concrete because of dehydration and hydration. However, halloysite shrinks irreversibly by losing two of its four molecules of water. It is possible, therefore, that this mineral, if present in aggregates, could contribute to drying shrinkage. K. Mather (12) believes that the presence of halloysite is fairly unlikely in aggregate in the United States. On the other hand, certain minerals of the second structural category, montmorillonite, vermiculite and perhaps other hydro-mica minerals, can take up interlayer water and expand. It appears also that, unlike base exchange in zeolites, base exchange in this type of clay mineral will cause volume change and may contribute to shrinkage or expansion in concrete.

Roy, Thomas, Weissmann and Schneider (13) observed that certain limestones had a rather high content of insoluble residue which was rich in mixed-layer clay minerals; also that some of these stones had high absorption capacities, in excess of two percent. They felt that these clay minerals might swell in the presence of water and cause distress in concrete made with such limestones as aggregates. They also suggested that illite might be altered to montmorillonite or a mixed-layer complex under conditions existing in concrete.

Mather (14) concluded that the available data indicated that 5 percent or less of kaolin clay in dense limestone aggregate may not injure the performance of the limestone as an aggregate, but that similar percentages of montmorillonoid clays in limestones with 1.5 to 2.0 percent absorption may produce a noticeable effect on the durability in freezing and thawing tests. Some of her identifications (12) of montmorillonite clays by optical means have proved to be incorrect on the basis of X-ray determinations of the same materials as clay-micas (illites). She stated "information is lacking on the mineral compositions of shales interbedded with limestone as that composition affects the performance of the aggregate." She also pointed out that not all of the shales are eliminated in processing and some exist in the smaller sizes of aggregate, which may cause pop-outs.

Rhoades and Mielenz (15) summarize some experience with expansions from clays and shales. They point out that particles containing clay minerals, particularly of the montmorillonite group or hydro-mica (illite) group commonly change volume significantly with wetting and drying. They observed that an altered dolerite containing 30 percent of the clay mineral nontonite expanded and contracted as much as 0.06 percent linearly during wetting and drying and that during repeated cycles of wetting and drying a permanent increase in length occurred. Concrete beams containing the dolerite as aggregate failed rapidly in freezing and thawing tests by expansion and loss of elasticity. They found that argillaceous limestones can expand more than 0.1 percent linearly with wetting from a dry condition and that some sandstones expand as much as 0.08 percent

linearly with wetting. For stratified rocks the volume change may be different in different directions. The argillaceous limestone used as aggregate in Chickamauga Dam, Tennessee, expands 0.028 percent linearly across the bedding and 0.016 percent parallel to the bedding during immersion in water. Where hydration results from hydration of montmorillonite clays, the volume change may be accompanied by pressures greatly in excess of the tensile strength of concrete.

In the early days of concrete, before suitable test methods and specifications were available, aggregates were, in many instances, taken from deposits close to the construction sites without testing for suitability as an aggregate in concrete. Viens (16) reports on the failure of a sidewalk which was in distress because of cracks and pop-outs. The coarse aggregate contained greenish pebbles that showed a distinct increase in volume and were found to be "dolomitic limestone bordering on a shale." He also reports on the concrete in a structure on Lake Huron which was in distress. This concrete was made from aggregate consisting of "debris of various formations of limestone, running from fairly pure limestone to dolomitic limestone, some containing chert and a form of iron." There probably have been many jobs with similar unsatisfactory service records in which the aggregates used would not meet present-day specifications. It seems that the two aggregates referred to above would have failed to meet the "Tentative Specifications for Concrete Aggregates," ASTM Designation C 33-61T, by failing in the "Tentative Method of Test for Soundness of Aggregates by Use of Sodium Sulfate or Magnesium Sulfate," ASTM Designation C 88-61T. Some of the aggregates used in the work reported by Holt probably would have been rejected by failing in the "Tentative Method of Test for Clay Lumps in Natural Aggregates," ASTM Designation C 142-55T. It seems certain the aggregates reported on by both Viens and Holt would have been rejected if examined in accordance with the "Recommended Practice for Petrographic Examination of Aggregates for Concrete," ASTM Designation C 295-54.

Because of the use of unsuitable aggregates these early failures were, of course, responsible for the development of test methods and specifications. Hence, a review of these failures is of little value in defining the extent to which these materials pose a problem today.

ORGANIC IMPURITIES

One of the early adverse experiences with organic impurities in aggregates occurred during the construction, during 1910-1911, of the Qinze and Kippewa Lake Dam on the upper reaches of the Ottawa River in Quebec by the Department of Public Works of Canada. Cameron (17) reported that when the work was nearly completed, it was observed that the concrete had not developed the expected strength. A study of the siliceous aggregate showed that the particles were coated with an organic material that was invisible to the eye, but which could be removed by washing with a 3 percent solution of sodium hydroxide. After this was done, normal strength concrete was obtained and this concrete showed no distress in 1937, whereas the concrete made with the unwashed aggregate had deteriorated to a degree that replacement would be necessary. Similar experiences probably could be avoided today by testing the aggregate in accordance with "Standard Method of Test for Organic Impurities in Sands for Concrete," ASTM Designation C 40-60, which was adopted as a tentative method of test in 1921. This method calls for treating the aggregate with a 3 percent solution of sodium hydroxide and comparing the color of the solution with that of a standard.

Bredsdorff, et al. (6) refer to work by F. S. Fulton, Concrete Technology—A South African Handbook, Johannesburg (1957) regarding contamination of aggregates with sugar because of the use of sacks previously used for sugar, and to a review by T. Karttunev and T. Sneck concerning the influence of humic acids in sands on the strength of concrete. They found that when the quantities of organic impurities in sands are to be estimated by the colorimetric test, it is common practice not to take into account the natures of the impurities. For this reason, they consider the test as unreliable.

The organic materials associated in nature with aggregates, besides vegetable matter such as leaves, grass, roots, and coal, are organic acids, such as humic and

tannic, and their derivatives. It has been pointed out that these do not present a problem with calcareous aggregates because the acids will react with the calcium carbonate of the aggregate to form innocuous calcium salts.

McNaughton and Nerbich (18) found that some sands in Canada contained organic material that acted as an air-entraining agent and yielded concrete with excessive air content.

Holt found that 48 of the 400 samples examined contained organic matter that delayed setting. Pieces of lignite, excess vegetation, leaves, grass, etc., were found in a few samples and one contained sugar derived from the sacks in which the aggregate was packed after washing. One coarse aggregate contained pieces that were coated with algae that affected the cohesion of the hardened paste to the aggregate.

SUMMARY

This review of the literature and in some cases unpublished experiences indicate that there are three classes of minerals that may combine with water in concrete and increase in volume. These are oxides, such as calcium and magnesium oxides, a zeolite (i.e., leonhardite), and clays of the montmorillonite category, such as montmorillonite and vermiculite.

Uncombined calcium oxide probably is never found in natural aggregates but has been observed in an expanded shale aggregate and in some blast-furnace slag and cinder aggregates. Clays and zeolite minerals have been found in rocks of both igneous and sedimentary origins.

The distress produced by these minerals as they combine with water in concrete is manifested either as spalls, pop-outs, overall expansion or low durability in freezing and thawing. There is a possibility that clays of the montmorillonite category might lose water during drying of concrete and be responsible for excessive shrinkage. It is possible to identify the oxides, zeolitic minerals and clay minerals by the procedures similar to those of ASTM Designation C 295-54 using X-ray DTA and electron microscopy. Hence, methods are available for identifying and estimating the quantities of these harmful minerals in aggregates.

Some natural sands and gravels have been found to contain organic materials that have either retarded the rate of setting, caused weak bonds between the hardened cement paste and the aggregate, or caused excessive entrainment of air. In some cases C 295-54 would reveal the presence of the harmful organic material and in others these materials would be revealed by C 40-60. Hence, it appears that methods are available for testing of aggregates, which if properly used, will almost eliminate the danger of producing unsatisfactory concrete because of the use of aggregates containing harmful amounts of organic materials.

ACKNOWLEDGMENT

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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 alkalies 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 alkalies 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 alkalies 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 alkalies 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 alkalies 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. Catherines, 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 colloidally 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.
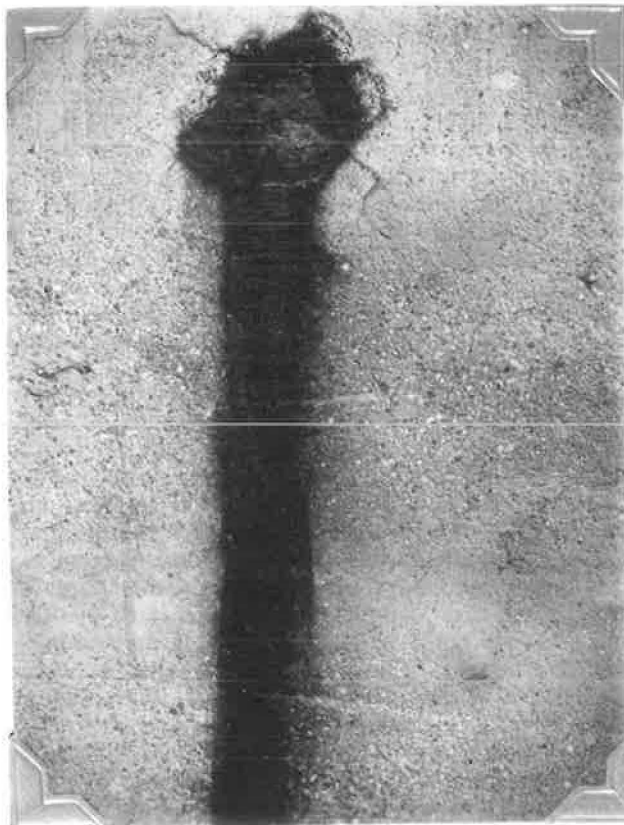

Figure 2. Surface of concrete retaining wall displaying staining and surface pitting produced by oxidation and hydration of pyrite in a particle of coarse aggregate. Magnification x $\frac{1}{4}$. (Courtesy of the Ohio Department of Highways.)
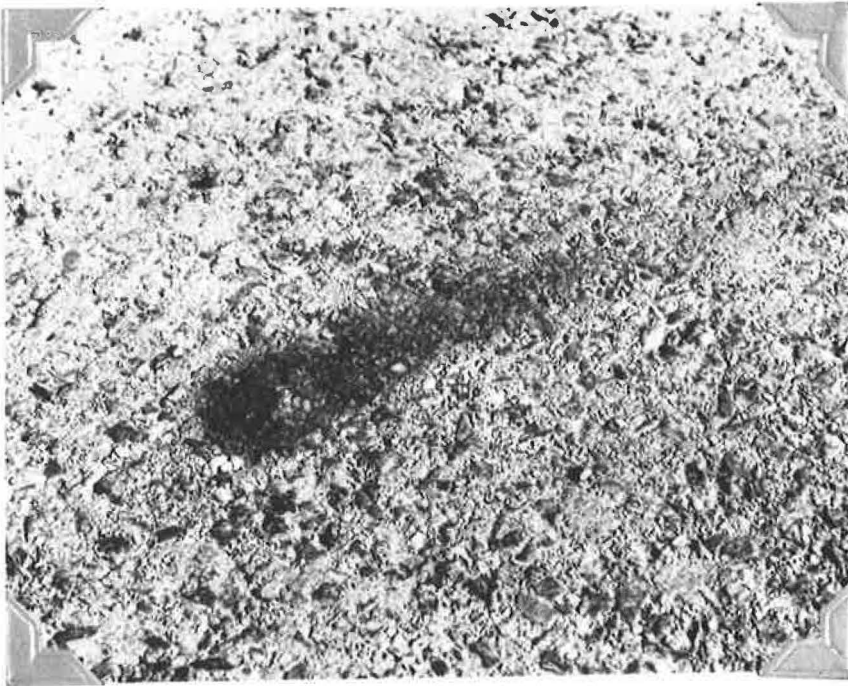
Figure 3. Iron oxide staining of bituminous concrete pavement as a result of oxidation and hydration of pyrite and marcasite in diabase coarse aggregate. (Courtesy of the Ontario Department of Highways.)

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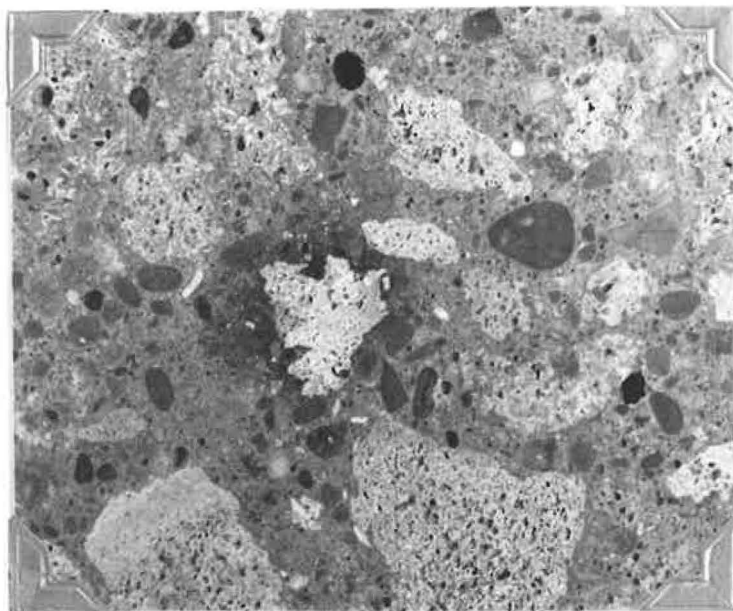
Figure 4. Dark green stain in cement paste surrounding a particle of air-cooled blast-furnace slag in coarse aggregate (natural size).

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, $CaSO_4 \cdot 2H_2O$, 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 sulfoaluminate 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 sulfoaluminate 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 SO_3) 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
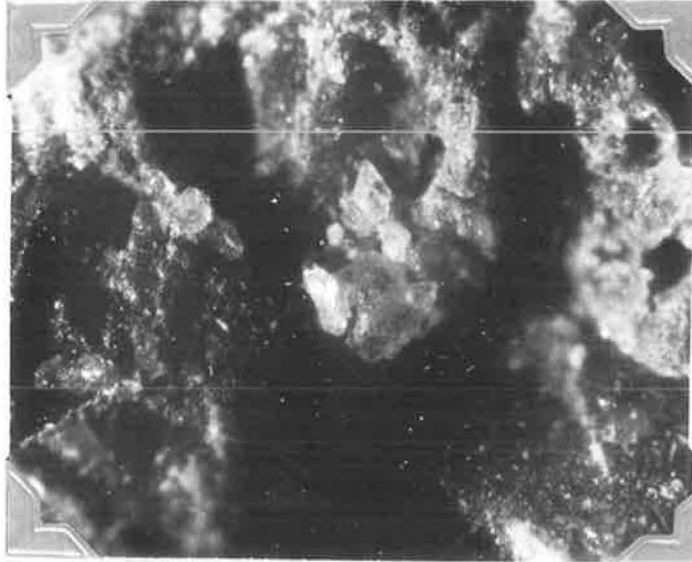

Figure 5. Gypsum crystals in weathered particle of air-cooled blast-furnace slag (magnification x 50).

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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