

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, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 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 generally 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 Qinzé 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. Sneek 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.

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