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Les premières études des problèmes de durabilité du béton découlant des effets de dilatation dus aux réactions entre certains granulats et les alcalis des ciments ont indiqué que l'opale et plusieurs autres types de silice plus ou moins amorphe étaient le composant réactif du granulat. Des recherches ultérieures ont démontré que d'autres types de roches pouvaient subir une expansion due à leur réactivité alcaline, et poser aussi des problèmes quant à la durabilité du béton. Les roches volcaniques vitreuses ou faiblement cristallines, les calcaires dolomitiques, les grauwackes, les phyllites et les argilites sont maintenant considérés comme pouvant être dangereusement réactifs. On a mis au point des essais normalisés qui consistent à mesurer les variations de longueur de barres de mortier, de prismes de béton et d'éprouvettes cylindriques de roche maintenues dans des conditions de température et d'hygrométrie constantes. On a effectué d'autres essais pour mieux comprendre le mécanisme d'expansion. On a réalisé, dans les premières phases de l'étude, des analyses géochimiques qui ont révélé que la géologie de la région était plus propice à des problèmes de dilatation que la géologie de la région.
Synopsis: Early studies of concrete durability problems resulting from expansive reactions between certain aggregates and cement alkalis implicated opal and other forms of poorly ordered silica as the reactive component in the aggregate. Later work showed that other types of rocks may expand in alkali and cause concrete durability problems as well. Glassy or poorly crystalline volcanic rocks, dolomitic limestones, greywackes, phyllites and argillites are now recognized as potentially deleteriously reactive. Standard tests were developed that involve the measurement of length-change of mortar bars, concrete prisms, and rock cylinders held under constant temperature and humidity conditions. Other tests have been used in attempts to gain a better understanding of the expansive mechanisms. Petrographic studies were carried out from an early date; with the introduction of more sophisticated equipment such as the scanning electron microscope, X-ray diffraction, and differential thermal analysis, petrography now plays an increased role in this area of engineering geology.

Keywords: aggregates; alkali-aggregate reactions; alkali-carbonate reactions; concrete durability; dolomite; expansion; limestone; petrography; reviews; siliceous aggregates
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INTRODUCTION

It is over forty years since the "classical" studies of alkali-aggregate reactivity were first published (1,2). Rocks and minerals found to be alkali expansive included opal and other disordered forms of silica and glassy or cryptocrystalline volcanic rocks. Standard methods of recognizing potentially deleterious alkali-expansive aggregates were developed and now include the mortar bar test (3), the concrete prism test (4), and the rock cylinder test (5). Other methods of measuring dimensional change such as the osmotic cell (6) and various dilatometers have also been used in studying the mechanisms of expansion. These test methods and their potential shortcomings have been reviewed by Grattan-Bellew (7). Petrographic investigations were carried out by Mather and Mather (8,9), and by Rhoades and Mielenz (10) among others, hand-in-hand with the development of dimensional change tests. The widespread introduction of X-ray diffraction, differential thermal analysis, and scanning electron microscopy greatly increased the power and versatility of these procedures.

Awareness of the serious damage caused by expansive alkali-aggregate reactions led to many more investigations of this type of concrete failure. More types of rocks came to be recognized as potentially deleteriously expansive, and the list now includes certain types of argillaceous dolomitic limestones, greywackes, phyllites and argillites. Some expand readily in alkali, others expand only slowly, and some have been reported to expand only after relatively long periods of exposure (11).

A number of factors have combined to make good quality aggregates in short supply close to places of intense urban development (12) and the temptation or necessity to use aggregates of lower quality is one factor that may contribute to the increased number of reported cases of durability failure due to alkali-aggregate reaction. Alkali-aggregate reactions are also affected by a number of factors in addition to type of
aggregate. These include the availability of alkalis, access to moisture, temperature, and the presence of admixtures in the concrete. The object of this paper is to review progress in understanding of the nature and occurrence of alkali-aggregate reactions.

**ALKALI-SILICA REACTION**

The rocks and minerals involved in this type of alkali-aggregate reaction include the vitreous, poorly-crystalline and strained forms of silica which occur in sedimentary, igneous and metamorphic rocks in the form of opal, chert, chalcedony and quartz. Although quartz is not generally associated with alkali-expansive behaviour, when strained by tectonic action (as in some quartzites) it may produce a slow but significant expansion which ultimately exceeds that of some cherts (Fig. 1). Expansion has also been found to result from use of some volcanic rocks, particularly when silicate glasses or cryptocrystalline minerals are present. In general, the expansion produced by these forms of silica is significantly slower than that caused by opal.

The mechanism of expansion is probably analogous to osmosis, but a semi-permeable membrane is not thought to be required. Siliceous gel formed by reaction between the cement alkalis and silica minerals sorbs water and exerts a swelling pressure. Factors that seem to affect the reactivity of silica include the degree of crystalline disorder, the micropore structure, internal strain, the nature of the cations in solid solution and other factors. The alkali-silica reaction has been studied in detail for longer than any other type of alkali-aggregate reaction.

**ALKALI-CARBONATE REACTION**

The alkali-carbonate reaction was first clearly described in the 1960's when it was recognized as an expansive mechanism probably different from that of the alkali-silica reaction (13,14,15). This conclusion followed from petrographic observations and behavioural differences during test. Known reactive rocks and minerals were absent and significant quantities of silica gel could not be found in deteriorated field concrete or laboratory test specimens that had shown large expansions. As well, there seemed to be no pessimum, and known inhibitors of alkali-silica expansion such as the well-known pozzolans were much less effective than anticipated and no effect at all resulted from the use of LiCl.

The new reaction resembled the alkali-silica reaction in that there was a marked dependence on available alkalis and water, temperature influenced the reaction, the type of cracking of affected concrete was similar and amount of expansion was influenced by particle size of the aggregate. After initial publication, detailed studies were carried out in a number of laboratories in Canada and the United States so that the number
of known localities where alkali-expansive carbonate rocks occurred increased rapidly.

At Kingston, Ontario, the alkali-expansive limestones are dense, medium-grey rocks with low porosity and absorption. In outcrops the rocks vary from thickly to thinly bedded, and while they are most typically grey they weather to a pale buff colour. There are thin, clay-rich layers and beds that are pale green and purple in colour (Fig. 2). On smoothly weathered or polished surfaces thin impersistent bedding (on the mm or cm scale) is often visible. Some of the rocks contain 1-2 mm pseudomorphs, possibly after halite or gypsum, that are now composed of a mosaic of calcite with some dolomite euhedra. Microscopic examination of thin-sections shows that the rocks are composed of dolomite, calcite, clay and small amounts of quartz and other detrital minerals. The dolomite occurs as euhedral crystals, sometimes zoned, that are about 50 \( \mu \)m and smaller in cross-section; the dolomite crystals are surrounded by a microcrystalline matrix of calcite in the 2-6 \( \mu \)m range. Areas of coarse-grained, clear sparry calcite are also present. Clay is common in the matrix, is sometimes partly enclosed within the dolomites, and may be somewhat concentrated near dolomite grain boundaries. Many of the observations made initially by optical means were subsequently confirmed by scanning electron microscopy (Fig. 3). The tight fabric that underlies the soundness and excellent physical qualities of this aggregate is almost certainly responsible, at least in part, for its alkali-expansivity. Similar rock is found in a quarry in Cornwall, Ontario (16). Mineralogical analyses made by X-ray diffraction methods showed that the dolomite is of the metastable variety, containing an excess of Ca above the ideal 50-mol percent together with Ca-Mg disorder and disturbed layer sequences normal to the c-axis. The calcite appeared to have reduced lattice spacings, suggesting the inclusion of a small proportion of ions such as Mg with a radius less than that of Ca. The clay minerals were found to be mainly illite, probably composed of more than one polymorphic form, and chlorite. Swelling clay minerals were absent. Differential thermal analysis in air and vacuum showed that organic material was often present in the acid-insoluble fractions and was probably intergrown with or adsorbed on the clay minerals (17).

Tests of the acid insoluble fraction by ASTM C289, the chemical method (18), gave some indication of potential deleterious alkali-silica reactivity, though the suggestion was far from conclusive (13). Opal is one of the most alkali-expansive forms of silica and attempts were made to find this mineral. The acid insoluble fraction of a number of expansive rocks was suspended in a liquid of specific gravity of 2.4. Only a very small amount of material could be separated by gravitational or centrifugal procedures, however, and analyses of
that residue by optical microscopy, differential thermal analysis, and X-ray diffraction failed to detect opal.

The expansivity of the rock was found to be extremely variable from bed to bed within a single quarry (Fig. 4) and even within different parts of the same layer of rock. Significant expansions may be recorded when the aggregate is made from some of the more reactive strata (Fig. 5), even when low-alkali cement is used in the concrete.

Dimensional change studies were also made with two types of dilatometer. In one, the combined volume of both powdered solid and alkaline solution was measured, i.e., the system was closed. In the other, the volume of the powdered solid was measured while the powder had access, via a porous plate of stainless steel, to water or alkaline solution in a separate chamber. Measurements were also made of flow of solution between the two chambers. Powders of expansive rocks and of mixtures of the same composition were studied in both types of dilatometer (19).

In the closed-system dilatometer all samples containing fine dolomite showed an increased volume, implying a density decrease in the total system - powdered solid plus alkaline solution. When the second type of dilatometer was used, volume increases were registered only when powdered expansive rocks were tested. There was also a flow from the chamber containing the alkaline solution into the chamber containing the powder. It was found that the total increase in solid volume decreased as the particle size of the powdered rock decreased. When mixtures were tested, no increase of solid volume or flow into the powder-containing chamber was registered.

Mineralogical studies had shown that alkaline attack results in a dedolomitization reaction: the replacement of dolomite by calcite and brucite (Mg(OH)₂) as solid phases while alkali carbonate forms in solution. In the above experiments with powders, the progress of this reaction was followed by dismantling of the dilatometers after increasing periods of time. Mineralogical changes in the solid were monitored by X-ray diffraction and differential thermal analysis, while changes in concentration of NaOH and Na₂CO₃ in solution were determined by titration. Several pieces of evidence indicated, however, that the dedolomitization reaction was not directly responsible for the problem.

Calculations indicated that the volume of the solid products detected was less than that of the dolomite being replaced; phase relations indicated that hydrated double salts, formed under some conditions, were unlikely to develop under the conditions in which expansion was found (13,14,20,21). When mixtures with the same composition as the expansive aggregate were dedolomitized in alkali, they showed an increase in total volume (solid plus liquid) but no increase in solid volume or inflow of solution. Thus, provided the dolomite crystals were small enough, there was...
a fairly rapid dedolomitization reaction in all cases but it was accompanied by an increase of solid volume only in the expansive rock. Decrease in the amount of expansion with decrease in particle size of the expansive rock further suggested that the fabric or texture of the material played a vital role in the expansive mechanism.

In other work, studies of adsorption isotherms had shown that the surface area and capacity for moisture retention of expansive rock was increased by treatment with alkali (22). This had led to the suggestion that brucite formed by the dedolomitization reaction was in the colloidal size range, with properties of an expansive water-sorbing gel. The suggestion had to be abandoned, however, because Fourier analysis of X-ray powder line profiles showed that the brucite crystals were within the upper range of the colloidal state and essentially the same in dedolomitized expansive rock and powdered mixtures. A different mechanism had therefore to be involved. It was proposed that dedolomitization of expansive rock releases dry clay that causes expansion by sorption of water (19). Support for this hypothesis was obtained by measurement of expansion of powder compacts and rock wafers exposed to stepwise increases in relative humidity or alkaline solutions (23).

The proposed mechanism accounts for the observed facts:

1) It explains why dedolomitization of mixtures caused no increase of solid volume in the dilatometer experiments since the clay residues were saturated before alkali was admitted to the system.

2) It accounts for the decrease in expansion with decrease in particle size of expansive rock, since fine grinding would release clay. Hence, pre-wetting of some clay would occur before dedolomitization.

3) Rock samples that are petrographically similar show varying degrees of alkali-expansivity (Figs. 4, 5). This may very well result from variation not only in the amount and nature of the clay but also in the extent to which the clay has been pre-wetted in nature.

4) The mechanism explains the absence of silica gel and other differences between this reaction and others. Conversely, similarities can be explained.

The hypothesis has received widespread but not universal support. For example, careful microscopic studies led Tang, Han, and Liu (24) to invoke dedolomitization as the direct cause of expansion. They suggested that the growth and rearrangement of the brucite crystals in the restricted space of the rock may be the key factor.
Limestones may, of course, contain disordered silica, and if used in concrete in which sufficient alkali is available they may cause expansion. Durability problems from this source have been recognized with increasing frequency in parts of Ontario and Quebec. A typical example is the Trois Rivières limestone, which petrographic examination has shown to be of fairly uniform composition. It is composed dominantly of pelletal biocalcarenite containing large fragments of bryozoans, brachiopods, fragments of crinoids and other fossil debris. Some of the limestone fragments are rich in intraclasts and others consist of calcisiltite (micrite) (Fig. 6). Scattered throughout the limestone are quartz grains (estimated to be less than 5%). Examination on the scanning electron microscope (SEM) has shown that the limestone contains large and small quartz grains that were identified by their X-ray spectra. Figure 7A shows a small grain of quartz or possibly cryptocrystalline silica. Fine silica was also found surrounding some calcite grains (Fig. 7B, C). This fine silica is thought to be the reactive component in the rock. Clay agglomerates were commonly observed in the insoluble residue obtained by dissolving the limestone in acetic acid (Fig. 7D). Figure 8A shows the energy-dispersive X-ray spectrum (EDXA) of the clay agglomerate; this may be illite since it is similar in appearance to the spectrum of that mineral (Fig. 8B). The EDXA spectrum of the silica particles showed some minor amount of Al, probably due to the presence of some clay platelets.

Expansion behaviour of concrete prisms (254 x 75 x 75 mm) made from Trois Rivières aggregate and cement from the Bath Plant of Canada Cement Lafarge Ltd. is shown in Fig. 9. The cement is type 10, with an Na₂O equivalent of 1.01%. Concrete was made with two levels of cement corresponding to 310 and 420 kg/m³. The results show that expansion of concrete prisms containing 420 kg cement was about double that of prisms containing 310 kg, indicating that this aggregate is very sensitive to the alkali content of the concrete. The aggregate is known to have caused severe deterioration of concrete structures in the Trois Rivières region (25). The importance of accelerated curing to identify reactivity of this type of limestone is underlined by the low expansion obtained when concrete was cured at 23°C if compared to that obtained when it was cured at 38°C. This shows clearly in Fig. 9. Figure 10 shows that the expansion attributed to limestone aggregate can be reduced by the addition of silica fume (SF) to the concrete.

ALKALI-SILICATE REACTION

Some silicate rocks have been suspected of causing durability problems due to expansive reaction with alkali ever since the early years of investigation of alkali-aggregate reactivity. Extensive studies of the low-grade metamorphic greywackes, phyllites and argillites of Nova Scotia were carried out in Canada during the 1960's at the request of the Nova Scotia Power Commission, who had observed movement and cracking in
concrete structures for over 30 years. A field survey of dam sites, bridge piers, retaining walls and foundation concretes showed widespread cracking of concrete (Figs. 11, 12), with strong indications of alkali-aggregate reaction. The evidence was complicated, however, by the effects of other agencies such as frost-action and by data indicating that expansion was very slow. Petrographic examination of field cores from affected concrete was carried out and rock types were selected for laboratory studies of dimensional change characteristics. Because of the slowness of the expansion, accelerating procedures were adopted.

The petrographic examination showed that the suspect rock types were greywackes, phyllites and argillites. The greywackes were composed of quartz and feldspar with accessory rock fragments (Fig. 3). The rocks were generally sheared and the crystals were commonly strained; mica-type minerals and argillaceous constituents were present in the matrices. The phyllites and argillites contained smaller amounts of quartz and feldspar of silt size in a matrix of layer-structure minerals showing varying degrees of recrystallization, shear and preferred orientation. These rock types were less abundant in the aggregates but nonetheless commonly present. Length change data showed that many were alkali-expansive (Fig. 1). Quartzites were also studied and were found to be composed of strained quartz, with some feldspar and accessory amounts of phyllosilicates. Only a few of the quartzites were alkali-expansive (26,27,28).

Rocks similar to those from the Appalachian province, which show alkali-expansivity, also occur in the north of Ellesmere Island, NWT (29), and from the Sudbury area of Ontario (30). Rocks of this type have therefore come to be looked upon as a possible cause of durability problems; evidence from South Africa and New Zealand supports this suggestion.

CONCLUSIONS

Until about ten years ago, particularly in countries outside the USA, there was a tendency among engineers either to disregard alkali-aggregate reactions completely or to consider that the problem occurred so rarely that to all intents and purposes it could be ignored. Since then it has become ever more widely accepted that expansive reactions between certain types of aggregate and alkali are a potential cause of serious durability problems in concrete. It is to be hoped that in the future many cases of durability failure from this cause will be avoided as a result of more general recognition and understanding of the nature of alkali-aggregate reactions.

REFERENCES

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Fig. 1--Length change of mortar bars (ASTM C 227) high-alkali cement
Fig. 2--Section of Pittsburgh Quarry, Kingston, Ontario, showing beds from which aggregate was obtained (Sample numbers are indicated in white in the center of the beds)
Fig. 3--Micrographs of dolomitic limestone from Kingston, Ontario, and greywacke from Nova Scotia
Fig. 4--Expansion of concrete prisms (254 x 75 x 75 mm) high-alkali cement aggregate, Pittsburgh Quarry, Kingston, Ontario

Fig. 5--Expansion of concrete prisms (254 x 75 x 75 mm) low-alkali cement aggregate, Pittsburgh Quarry, Kingston, Ontario
Fig. 6--Optical micrographs of Trois Rivieres limestone showing fossil fragments, intraclasts, and matrix of calcisiltite
Fig. 7--Scanning electron micrographs of Trois Rivieres limestone (polished and etched 2 percent acetic acid, 5 minutes plus 2 hours ion milling)
Fig. 8--Energy dispersive X-ray spectrum of clay agglomerate in acid-insoluble residue, Trois Rivieres limestone, compared to that of illite
Fig. 9—Effect of w/c, cement content and storage temperature on expansion of concrete prisms (254 x 75 x 75 mm) — aggregate, Trois rivieres limestone

Fig. 10—Effect of silica fume (SF) on expansion of concrete prisms (254 x 75 x 75 mm) containing 420 kg cement/m³ concrete, w/c 0.45 — aggregate Trois Rivieres limestone
A--Mallay Falls, power station

B--Malay Falls, power house, downstream side

Fig. 11--Photographs of concrete structures showing durability problems, Nova Scotia, Canada
A--Malay Falls, power station

B--Harmathy Power House

Fig. 12--Photographs showing detail of concrete durability problems, Nova Scotia, Canada
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