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A NEW APPROACH TO THE STUDY OF ALKALI-AGGREGATE REACTION MECHANISMS

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ABSTRACT

The reactions involved at the interface between three well-known reactive aggregates and high alkali cement pastes, and the consequent formation of secondary reaction products, were studied using a simple two phase system consisting of cement paste cast in contact with a polished surface of aggregate particles. Applications to the study of alkali-silica and alkali-carbonate reaction mechanisms are presented.

1. INTRODUCTION

The alkali-aggregate reactivity in concrete was first identified about fifty years ago. Since then, considerable efforts have been and are still being made for the better understanding of the mechanisms involved. This paper describes a method for the study of the reaction mechanisms occurring at the interface between reactive aggregates and high alkali cement pastes. In this method, concrete is represented by a simple two phase specimen, called a "composite-sample", consisting of a cement paste cast in contact with a polished surface of a single aggregate particle [1]. In concrete, it is usually difficult to locate precisely and consequently to analyse the interfacial zone. The proposed method presents a great advantage since the surface to be examined is a perfect plane.

2. DESCRIPTION OF THE METHOD

The method was developed to study the process of hydration of cement paste in the close vicinity of aggregate particles [1]. It allowed identification of an interfacial zone, called "transition zone", which presents distinct characteristics with respect to the bulk cement paste. Indeed, a zone of porous cement paste is created with a relatively high water content which promotes the diffusion of ions and formation of larger hydrate crystals. This transition zone was confirmed by different methods, including abrasion testing on composite-samples [2], as well as SEM observations on typical concretes [3]. All these methods established that, within a few tens of micrometers, the porosity of the cement paste progressively decreases from the aggregate interface towards the bulk cement paste. The experimental procedure involves the casting of cement paste in contact with a polished surface of an aggregate particle (Fig. 1). At specified times, specimens are broken along the interface. The internal surfaces of both halves can then be studied by optical microscopy, XRD, EMPA and SEM-EDXA.

3. MATERIALS AND EXPERIMENTAL PROCEDURES

The cement used in this work was a type 10 high alkali cement (1,04% Na_2O equivalent). For each of the three reactive rocks tested, 10 cores (2 cm dia. x 2 cm long) with one polished basal surface were individually placed in a PVC tube of the same diameter. A cement paste (with a 0,3 w/c ratio) was then cast over the polished surface of the cores. The tubes were then sealed and stored in a hermetic container for 24 hours (100% R.H., 23°C). After this curing period, the composite-samples were demolded, returned to the hermetic container and stored in a small laboratory oven (38°C). At specified times, samples were removed from the oven, and broken along the interface between the aggregate and the cement paste. The two halves were then analysed by SEM-EDXA and XRD. Thin sections taken perpendicularly to the interface in unbroken composite-samples were also examined by optical microscopy (Fig. 1).

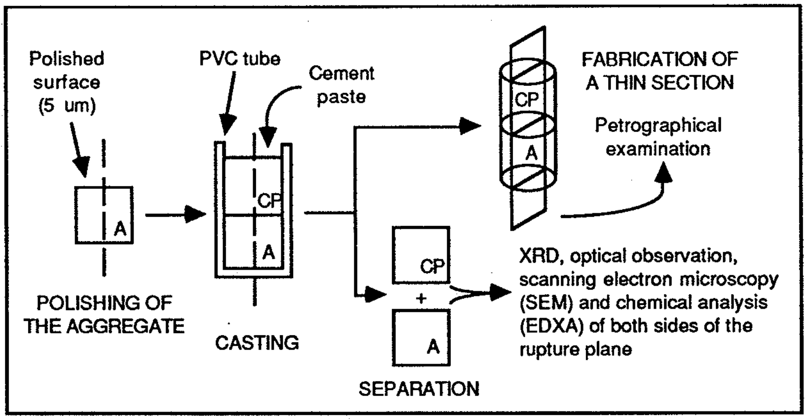


Figure 1 - Method to study the interfacial zone between cement paste and aggregate particles.

4. OBSERVATIONS AND RESULTS

4.1 Classical Alkali-Silica Reactivity - Opal from Massif Central (France)

This very reactive material is composed of low temperature trydimite, quartz, and traces of chlorite, calcite, dolomite and feldspar. It has been already used in an extensive laboratory study of alkali-silica mechanisms [4]. The reactions between the cement paste pore solution and this opal proceed rapidly. The "reaction front" progressively extends from the original interfacial plane, and into the aggregate core, thus forming a zone of weakness along which preferential fracturing may occur. After only three days of curing at 38°C and 100% R.H., massive silico-calco-alkaline gels, locally supporting fragments of "partially reacted" opal, were observed on the broken surface corresponding to the cement paste side (Figs. 2 and 3). "Reacted opal" (e.g. containing a few percent K and Ca) was observed on the aggregate side of the broken surface . Figure 3 shows a surface corresponding to the cement paste side of a 14 day old composite-sample, with EDXA analyses at two points on this surface.

XRD and SEM-EDXA analyses suggest that the alkaline attack of particles susceptible to classical alkali-silica reactivity involves progressive and "in situ" transformation of the siliceous mineral into amorphous silico-alkaline gels. This transformation promotes the softening of the reactive siliceous particle, and the rupture plane tends to run at the interface between reacted (gels) and partially reacted silica. This rupture plane then progressively moves, from the initial cement paste/aggregate interface, into the aggregate particle.

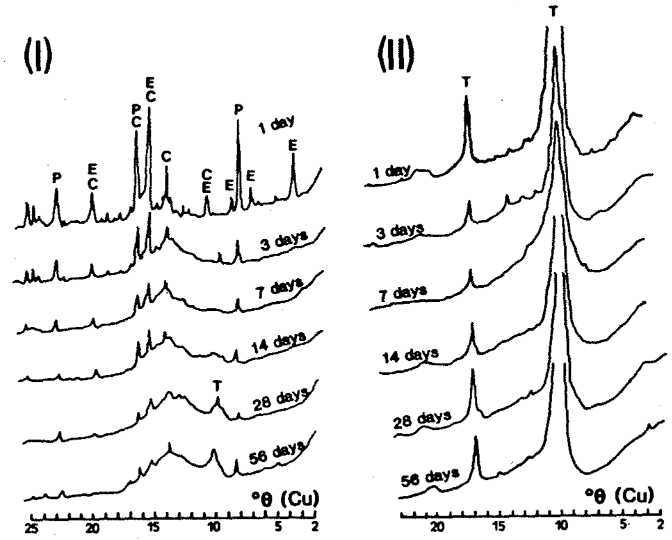


Figure 2 - XRD on the cement paste (I) and aggregate (II) sides of broken composite-samples with opal.

P = Portlandite
E = Ettringite
C = C_3S and/or C_2S
T = Tridymite

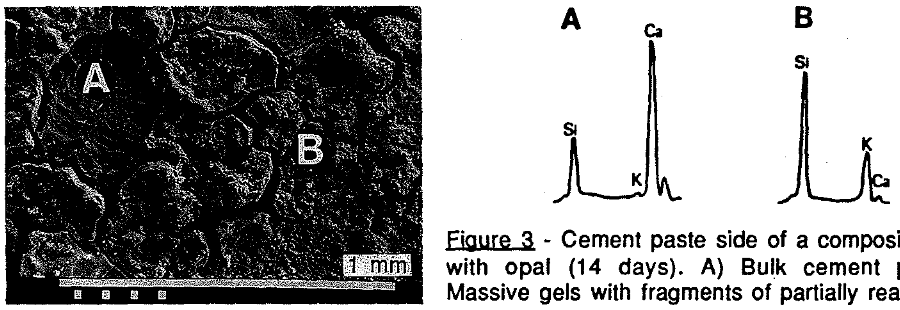


Figure 3 - Cement paste side of a composite-sample with opal (14 days). A) Bulk cement paste. B) Massive gels with fragments of partially reacted opal.

4.2 Slow/Late Expanding Alkali/Silica Reactivity - Potsdam Sandstone from Quebec (Canada)

The Potsdam sandstone produced major problems in concrete structures from the Beauharnois Channel (Quebec, Canada) [5,6,7,8]. A quartzitic cement in optical continuity (syntaxial overgrowths) with well-rounded quartz grains of igneous origin (Fig. 4) is thought to be the reactive component in this rock. Indeed, a core sample identical to those used for the composite-samples, and soaked in a 3N NaOH solution at 80°C, confirmed the selective attack of this quartzitic cement (Fig. 5A). The sample showed almost complete disaggregation within 3 weeks. Observations in thin sections indicate that the quartz grains contain many tiny fluid inclusions which also constitute preferential sites for corrosion by alkaline solutions (Fig. 5B). In contact with the cement paste, using the composite-sample method, a typical arrangement of hydrates is first observed in the transition zone [1], with large crystals of portlandite parallel to the interface. Adjacent to this is a porous zone which consists of a loose arrangement of portlandite, ettringite and CSH (Fig. 6). In the presence of the cement paste pore solution, the siliceous cement has been progressively attacked with the consequent formation of silico-calco-alkaline gels in the new-formed intergranular pores (Figs. 6 and 7).

These observations confirm the chemical instability of the quartzitic cement in the Potsdam sandstone. The availability of calcium is a critical factor for the formation of gels, since an aggregate particle which is not in contact with cement paste (in a NaOH solution) is only disaggregated as a result of selective dissolution of the quartzitic intergranular cement.

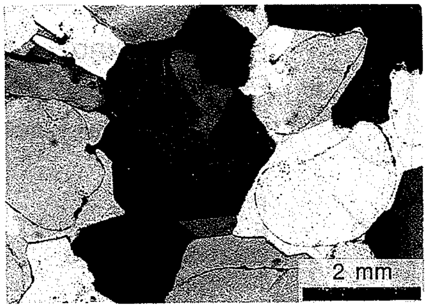


Figure 4 - Well-rounded quartz grains of igneous origin cemented by quartzitic cement in optical continuity (syntaxial overgrowths) (Potsdam sandstone).

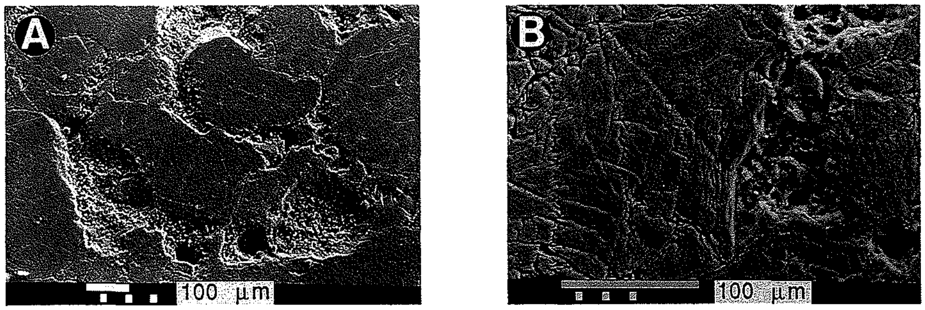


Figure 5 - Corrosion of the quartzitic cement (A) and etching pits at the surface of quartz grains (B) (Potsdam sandstone, 2 weeks in 3N NaOH solution at 80°C).

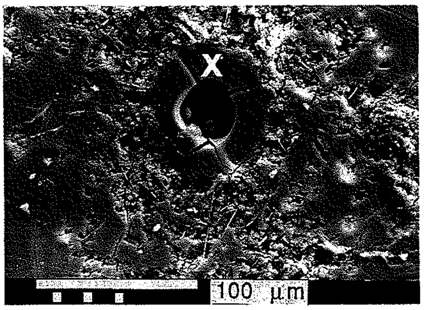
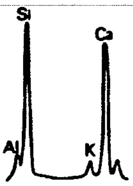


Figure 6 - Cement paste side of a composite sample with the Potsdam sandstone (56 days). A loose arrangement of hydrates is observed within the transition zone.



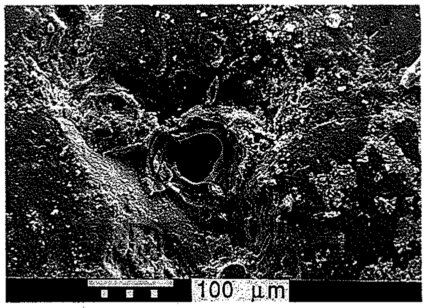


Figure 7 - Gels filling empty spaces resulting from selective attack of the quartzitic cement (composite-sample with Potsdam sandstone, 56 days).

4.3 Alkali-Carbonate Reactivity - Dolomitic Limestone from Ontario (Canada)

This argillaceous dolomitic limestone from the Gull River Formation is responsible for severe deteriorations of many concrete structures in the vicinity of Kingston (Ontario, Canada) [9]. In spite of numerous research studies since the beginning of the sixties, the deleterious reaction/expansion mechanisms associated to this rock in concrete are still not well known. The observation of a two years composite-sample involving a very reactive rock sample, selected in the Pittsburg quarry (Ontario, Canada) by Dr. P.E. Grattan-Bellew from NRCC (Laboratory #78-16), reveal some interesting features. Large amounts of secondary calcite crystals are observed in the transition zone between the aggregate and the bulk cement paste. This phenomenon, observed in thin section (Fig. 8) and under the SEM-EDXA system (Fig. 9), is likely a result of dedolomitization. On the cement paste side of the composite-sample, this well-formed calcite is in association with portlandite and CSH. On the other hand, on the aggregate side of the broken surface, the calcite grains are closely associated to a magnesium-rich thin film showing numerous microcracks (Fig. 9), assumed to be brucite ($Mg(OH)_2$). This film seems to coat dolomite crystals and illite. This magnesium-rich phase was not observed on the cement paste side of the composite-sample.

These observations indicate that calcite, a known product of the dedolomitization process, can precipitate at relatively large distances from the reaction sites. The phenomenon would then be a dissolution-diffusion-precipitation mechanism. Brucite which is relatively insoluble compared to calcite under high pH conditions, seems to be closely asociated to the dolomite grains (as a deposition product after Mg solubilization or as an "in situ" solid residue from dedolomitization). These results also confirm petrographic observations on concrete laboratory prisms affected by alkali-carbonate reaction, in which beige secondary thin rims are often observed surrounding aggregate particles. These rims were identified under the SEM-EDXA as secondary and well-formed calcite crystals. These crystals are closely associated to dedolomitization, since they have never been observed in deteriorated concretes containing alkali-silica reactive limestones from many areas of the St. Lawrence Lowlands [10].

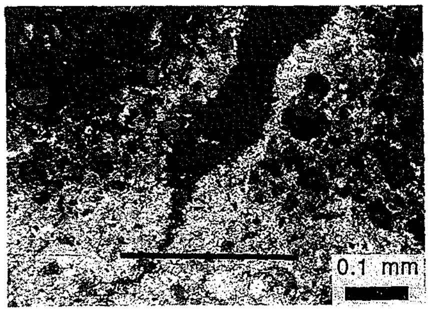


Figure 8 - Secondary calcite deposits within the transition zone between a Kingston aggregate particle and the cement paste. The straight line corresponds to the original polished surface of the aggregate particle. (Composite-sample, 2 years).

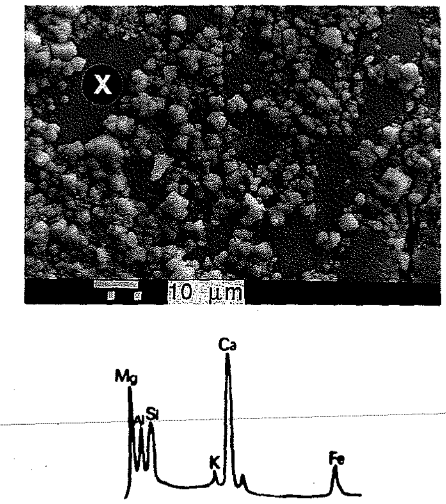


Figure 9 - Aggregate side of a composite-sample with the Kingston limestone (2 years). Secondary calcite is closely associated with a Mg-rich thin film assumed to be brucite.

5. CONCLUSION

The results presented above confirm the usefulness of the composite-sample method to study alkali-aggregate reaction mechanisms. The following conclusions are consistent with the observations made in this study:

1) Classical alkali-silica reaction involves the "in situ" disorganization and the transformation of reactive silica into amorphous gels. These mechanisms progress with time deeper into the silica.

2) The various silica phases which can coexist in a given aggregate may be differentially attacked by the cement paste pore solution, according to their chemical, mineralogical and crystallographic characteristics, but also to their origin and geological history. For instance, the sedimentary quartz cement in the Potsdam sandstone is selectively attacked, even if it is recrystallized in optical continuity with the detrital quartz grains of igneous origin.

3) The dedolomitization process involved in the alkali-carbonate reaction seems to produce very thin films of brucite directly at the surface of the dolomite grains (precipitation or solid residue) and precipitation of idiomorphic calcite, sometimes at considerable distance from the reaction sites. In normal concretes containing alkali-carbonate reactive aggregates, the calcite forms rims around the aggregate particles and maybe be involved in the concrete expansion. It is noted that such rims were never observed associated to alkali-silica reactive limestones of the St. Lawrence Lowlands.

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