Microstructure of Reaction Products

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ABSTRACT

The major Alkali Aggregate Reaction products include siliceous gels either massive or textured gels and crystals in lamellae or fibers. Microstructure of cracked concretes, as observed by light and electron microscopy, shows a weak cement paste - aggregate bond. Elemental analysis by EPMA or EDAX of this interface reveals ionic diffusion of alkalies but also of calcium carbonate and sulfate which gives rise to secondary minerals as hydrocalcite, ettringite and thaumasite.

INTRODUCTION

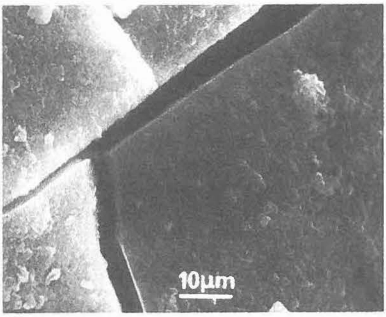
The alkali aggregate reaction produces gels and crystals which can vary in elemental composition but appear alike in many deteriorated structures. Amorphous and crystalline products occur at the aggregate-cement paste interface in a dark rim and white deposits in siliceous aggregates or in a white rim in dolomitic aggregates. They also fill in cracks and pores of both aggregates and matrix and exude at the concrete surface. This paper will report data on the microstructure of the reaction products studied by electron optical methods and X-Ray diffraction. Two Hydro-Québec dams, Beauharnois (sandstone aggregates) and Les Cèdres (dolomitic aggregates) will be given as examples of a SEM examination.

MICROSTRUCTURE OF GELS

Gels are silicates more or less alkaline. After chemical analyses of extracted and synthetic gelatinous products (Gutteridge & Hobbs, 1980) or SEM and EPMA data on dried concrete samples (Bérubé & Fournier, 1986), these gels contain about : 56 - 86 % SiO_2 , 2 - 8% K_2O, 0.4 20 % Na_2O, 1 - 28 CaO, 10 - 30 % H_2O.

1. Massive gels

Massive and isotropic gels deposited on siliceous aggregates and appearing with conchoidal drying cracks under SEM examination (fig.1) constitute the dark rim easily observed on concrete sections. Very often the gel seems to achieve a pseudomorphis of the aggregate (Regourd, Hornain, Poitevin, 1981). This silicate contains potassium and calcium but with a low CaO/SiO_2 ratio (0.1 to 0.5). The elemental composition as determined



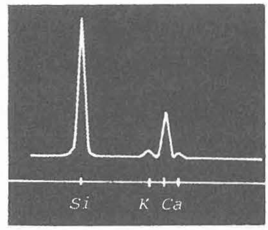
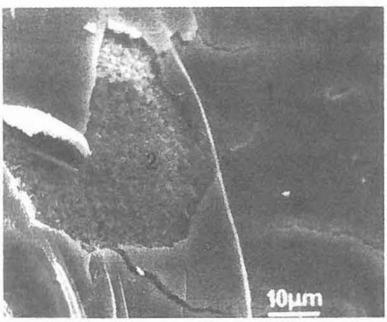


Fig.1 Massive gel on siliceous aggregate (Les Cèdres)



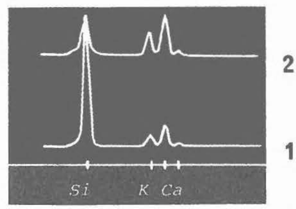


Fig.2 Isotropic gel (1) and fine grained product (2) (Beauharnois)

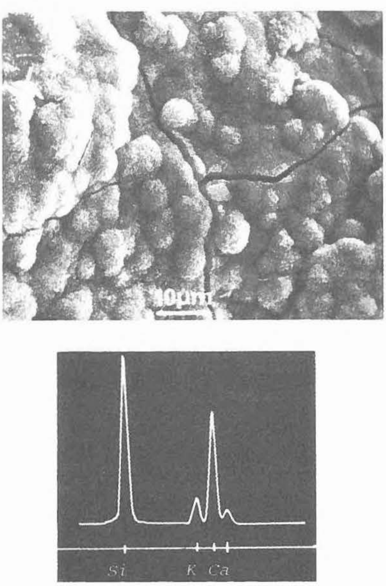


Fig.3 Spongy layer (Beauharnois)

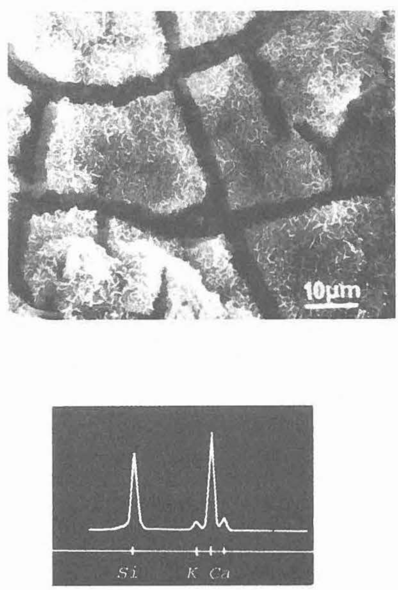


Fig.4 Foliated coating (Les Cèdres)

by EDAX varies from one point to another in the same sample. As differences in the SiO_2/Na_2O ratio lead to a difference in the gel viscosity (7,8) isotropic alkaline silicates are found in the matrix far from aggregates. A complete gelification of the cement paste was observed in mortars showing an "explosive" expansion due to the alkali reaction of opal grains (Liu, 1986). Gel solidification around opal particles revealed by microhardness measurements has been attributed to the incorporation of calcium ions (Kawamura, Takemoto, Hasaba, 1983). Gels are also located in cracks and pores of the cement paste where they are enriched in calcium (C/S = 1.2-1.4). Superposed layers of different composition and texture have been observed. They are either clear and porcelain gels in pores (Bérard & Lapierre, 1977) or isotropic and birefringent fine grained materials in cracks (St John, 1985).

2. Textured gels

With time, a massive gel can develop a texture, grainy (fig.2) or spongy (fig.3) or foliated (fig.4), always related to an increase in calcium ions. Textured gels have been observed in dams at Beauharnois and Les Cèdres. Spongy and foliated gels also exhibit large drying cracks (fig.3) and 4). The globules (fig.5) named botryoids (Bérubé & Fournier, 1986) have a different composition in the Beauharnois dam containing Postdam sandstone and in the Les Cèdres dam containing dolomitic limestone. The botryoidal spongy silicate is richer in calcium when in the presence of calcerous stone. Calcium ions could come from both the cement paste and carbonate aggregates. Foliated gels are not very different from those of the C-S-H in the cement paste. On the surface of massive gels in the Beauharnois dam appear **rhombohedral** crystals of calcite (fig.6). Bérard and Lapierre (1977), also observed calcite and hydrocalcite in presence of the Postdam sandstone which is a polyphased rock containing an orthoquartzite as the reactive material.

MICROSTRUCTURE OF CRYSTALS

Crystalline products related to the alkali-aggregate reaction have been characterized by SEM and XRD.

1. SEM examination

Among different crystalline products, Davies and Oberholster (1986), noted three distinct types namely rod-like, blade-like and rosette-like crystals. Various crystals have been found in canadian dams at Beauharnois and Les Cèdres.

- *rose crystals*

The rose crystals are alkaline silicates containing Al (fig.7). After Bérubé and Fournier (1986) who observed them in presence of quartzite, their composition is relatively stable compared to that of gels :
56 - 63% SiO_2 , 20 - 27% Al_2O_3 , 8 - 11% K_2O, 6 - 8 % Cao
The Al ions could come from both feldspars or chlorites and cement paste.

- *lamella crystals*

Lamella crystals (fig.8) can be close in composition to rose crystals except for their Al content. They sometimes appear flexible. The lamella observed in the Beauharnois dam contain a large amount of sodium ions which could be partly provided by deicing salts as suggested by Bérard and Lapierre (1977).

- *fiberous crystals*

Fiberous crystals are potassium calcium silicates (fig.9). Compared to the other crystalline products they have the lowest amount of silica (Davies & Oberholster, 1986). Heaped ettringite rich in SiO_2 or thaumasite are localized either at the aggregate border or in pores and cracks of the cement paste. These fibers were easily seen in Les Cèdres dam.

- filament and needle crystals

Flexible filaments emerge from a spongy gel (fig.10). Liu (1986) called them "silk threads" considering that they solidified after extrusion from closed pores opened during the sample preparation for microscopic observation.

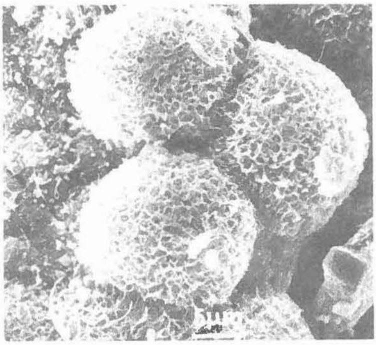


Fig.5 Botryoidal silicate (Les Cèdres)

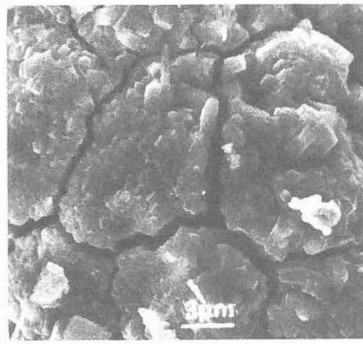
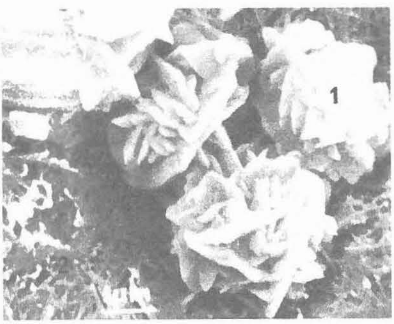


Fig.6 Massive gel and calcite microcrystals (Beauharnois).



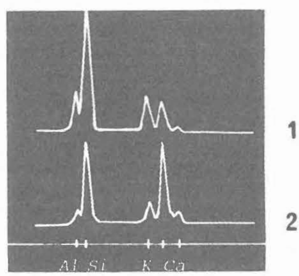


Fig.7 Rose crystals (1) (Beauharnois)

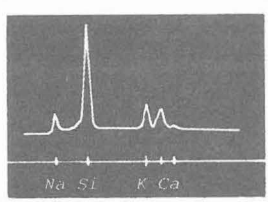
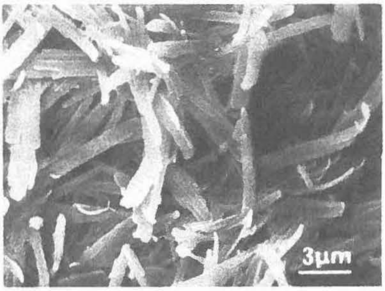


Fig.8 Lamella crystals (Beauharnois)



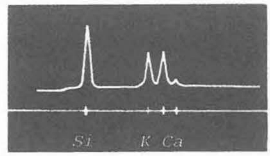


Fig.9 Fiber crystals (Beauharnois)

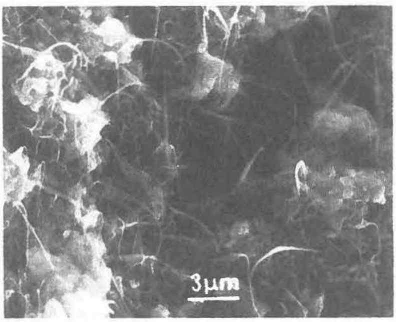


Fig.10 Filament crystals emerging from a spongy gel (Les Cèdres)

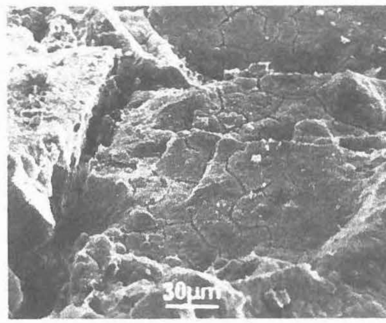


Fig.11 Silicate gel on a dolomitic aggregate largely fractured (Les Cèdres)

2. XRD Analysis

Crystals scraped from concrete and analysed by XRD exhibit numerous peaks. Three of them at around 12 Å, 8 Å, 3 Å seem to belong to three phases. Davies and Oberholster (1986) tried to isolate the different crystalline phases by a heat treatment. The 12 Å peak disappeared at 140°C after a reversible shifting at 7.2 A which was related to a loss of water. The 8 Å and 2.9 Å peaks disappeared respectively at 300 and 400°C and were replaced by a halo of an amorphous material. A 600°C a new XRD pattern occurred which could characterize trikalsilite K_{07} $Na_{0.3}Al\ SiO_4$, silleyite $Ca_5Si_2O_7\ (CO_3)_2$ or margarite $Ca\ Al_2\ (Si_2Al_2)\ O_{10}\ (OH)_2$. Treated samples observed under SEM examination lead to the conclusion that the rosette-like phase is characterized by the 2.9 Å peak.

DISCUSSION

Both examples of concrete deterioration reported here have to be related to a silica reaction producing gels and crystals. Although the Les Cèdres dam was built with dolomitic aggregates there was no white rim around them which could have been due to dedolomitisation with formation in three layers of brucite, calcite, carboaluminate and magnesium silicate (Poole, 1981) However a decohesion of the stone with large cracks and isolated dolomite rhombs in the calcite matrix was clearly observed. Debris were covered with silicate gels (fig.11) generated by the Postdam sandstone which can reach 20% in this dolomitic rock (Bérard & Roux 1986).

Mechanisms of the formation of alkali aggregate reaction products involving expansion of concrete have been explained in different ways. Poole and Al-Dabbagh (1983) consider that the gel/solution interface is an elastic osmotic membrane which can swell slowly forming a series of rounded domes. If the reaction is more rapidly produced as at high temperature, the membrane splits and the gel spills out as a sheet or foil. The frequent splits in the membrane lead to a sponge-like mass of plates and foils. The same theory is proposed by Liu (1986) for the "silk threads" formation. According to St John (1985) and Davies and Oberholster (1986), the first product formed is the isotropic gel which fills cracks preexisting in aggregate before their use in concrete. The massive gel prevents the crack from closing and the widening of the crack leads to the fracturing of concrete. However, the role of various ions such as K^+, Na^+ , OH^- Ca^{2+} and also CO_3^{2-}, Al^{3+}, Fe^{3+}, SO_4^{2-} , Cl^- which diffuse through the pore solution must be pointed out. Calcium hydroxide which forms in direct contact with aggregates in the first stage of the cement hydration seems a necessary prerequisite for the development of destructive reactions as shown recently by Chatterji, Thaulow, Christensen and Jensen (1986). The alkali aggregate reaction gives rise to various primary and secondary products and can be regarded as a complex process which still calls for research. More studies are needed on the nature and amount of ions provided by polyphased aggregates in an alkaline solution or in the pore solution of the cement paste. The presence of ettringite and thaumasite may be of significance in accelerated tests which are now being introduced and which are sometimes unsuccessful (Grattan-Bellew, 1983).

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