

POP-OUT FORMATION AND BULK CRACKING OF CONCRETE INDUCED BY CALCAREOUS METAMORPHIC AGGREGATES IN TROPICAL ENVIRONMENT

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ABSTRACT

Concretes from buildings in hot and wet environmental conditions were studied by optical (reflected and transmitted light), scanning electron microscopy (SEM) and X-ray diffraction (XRD). These concretes show two types of deleterious AAR in relation with the use of aggregates containing silicates coming from metamorphism of calcareous rocks in contact with a magma: wollastonite, prehnite, cryptocrystalline clayey products containing silicon and magnesia. The high reactivity of the latter leads to rapid formation of pop-out and bursting of aggregates due to formation of a nearly pure alkaline gel having a low viscosity. In some cases these aggregates have led to bulk cracking of concrete by formation of a viscous gel containing silicon, potassium and calcium. An attempt is made to link up both the phenomenons to the basic mechanisms of AAR.

Keywords : Alkali-silicate-reaction, pop-outs, bulk cracking, stevensite, wollastonite

INTRODUCTION

During the last five years, an important number of constructions on the Saint Martin Island (French West Indies) have been affected by alkali-aggregate reactions (AAR). The involved structures are especially hotels and a water reservoir constructed at the end the of 80s.

The geographical location of the Saint Martin Island, situated to approximately 200 km to the North West of Guadeloupe Island confers it a climate of tropical type, characterized by an average temperature around 27 °C with maximum higher than 35 °C and an average relative humidity of approximately 75% reaching sometimes 90%. In addition, external building parts are exposed to strong tropical rains, to surface run-off with periods of sunshine and intense evaporation. Moreover, due to the insular character, buildings are never totally protected from marine influence and building materials (mixing water, sand..) cannot be totally free from marine pollution. All these environmental conditions increase the risks of AAR.

The most frequently observed damages are pop-outs which occur on the structure surface (Fig. 1). Pop-outs may be accompanied by bulk cracking due to internal swelling of concrete (Fig. 2). These two types of damages can be associated to efflorescences, exsudations, discolorations and blistering of paints.

Pop-outs consist of detachment of conical portions from the concrete surface. The cones are several millimeters high with a deleterious aggregate in the base of the pit. Alteration of the aggregate and gel formation lead to a volume increase, local stress and bursting.

Pop-outs can be observed on all type of structures submitted to high humidity conditions, but in this case, they were mostly observed on the bottom part of staircases, floors or slabs. They often have appeared very quickly, approximately one year after construction. This rapid kinetics of reaction was confirmed by the occurrence of pop-outs on cores surface after unwrapping from the cling-film used to preserve them from desiccation and carbonation after coring.

AAR in plain concrete often produces a cracks pattern showing a roughly hexagonal network corresponding to internal swelling of concrete. In reinforced beams, the cracks can form along the length of the beam reflecting the pattern of the underlying steel. Cracks are often associated to pop-outs, but pop-outs can exist without bulk cracking.

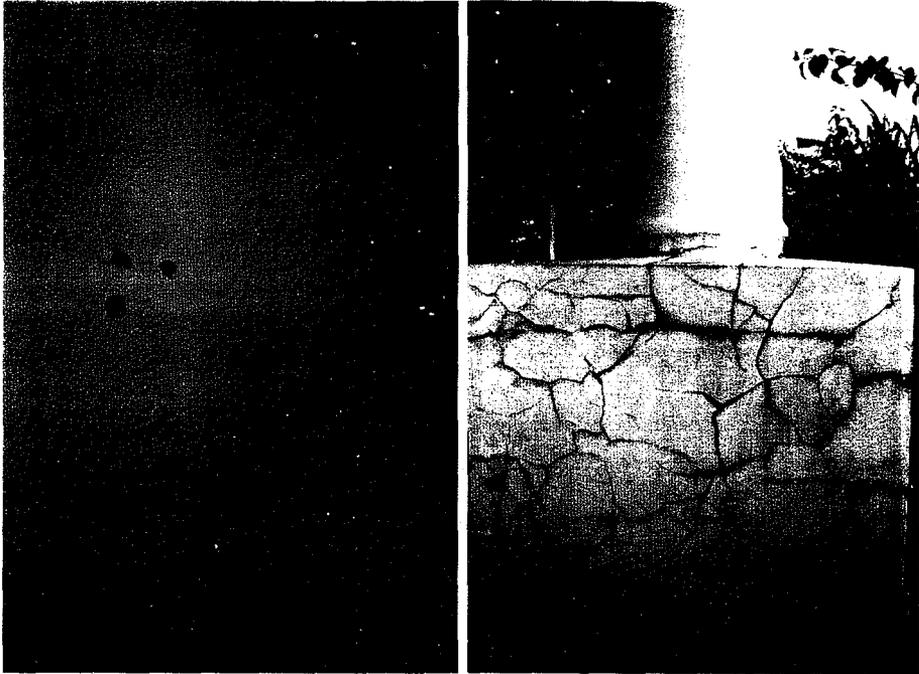


Fig. 1 Pop-outs observed on the bottom part of staircase
Fig. 2 bulk cracking observed on column base

GENERAL CHARACTERISTICS OF CONCRETES

The different examinations and analysis carried out on cores extracted from damaged structures show that all concretes have compositions close to each other. They are made up of OPC, calcareous sand and angular silicon-calcium gravel. The sand is mostly a marine sand formed by microcrystalline clayey calcite and containing a large amount of bioclasts. The high porosity of the bioclasts increases the porosity of the concrete itself. The coarse aggregates, coming from different quarries of this island, are microgranular or aphanitic melanocratic igneous rocks and multicoloured or green dominante colour silicon-calcium rocks. These green aggregates are particularly abundant in deteriorated concretes.

The concretes often contain a high amount of active alkaline oxides always above 3.4 kg/m^3 which can reach more than 10 kg/m^3 especially in zones close to the structure surface. They also contain sodium chloride coming from marine environment and from sand which can promote AAR [Nixon *et al.*, 1986]. In concretes under study, the chloride amount can reach 0.2 %. Their porosity is often higher than 20% corresponding to a low compactness. Their mechanical strengths are around 20 MPa.

PETROGRAPHIC CHARACTERISTICS OF THE AGGREGATES

The Saint Martin Island is one of the link of the ancient insular arc of the Lesser Antilles. Approximately one half of its area is formed by magmatic rocks of volcanic or plutonic origin. These rocks are exploited for aggregate production. The volcanic rocks belong to the andesitic series : basalts, andesites and dacites, while plutonic rocks are quartz diorite type. Andesites are often associated to dioritic formations corresponding to faster cooling. Magmatic rocks, especially quartz diorites dated Oligocene (35 My) are in most cases of intrusive type in the Eocene (≈ 40 My) formation of "La Pointe Blanche" made up of pyroclastic tuffs and limestones. These magmatic rocks intrusion has led the mineralogical and chemical transformation of the surrounding tuffs, with appearance, especially, of epidote. This mineral easily identifiable by the green colour it gives to the rocks, is very frequent in many points of the island. Furthermore, tuff and intrusive rocks have undergone metasomatic transformations (exchange with the external environment through hydrothermal fluids) leading to a burying metamorphism (Westercamp *et al.*, 1980).

The petrographic nature and the detailed mineralogical composition of the rocks have been determined by thin sections examination under polarizing microscope, powder and oriented preparations X-ray diffraction (XRD) and scanning electron microscope (SEM). These different analysis have been carried out on concrete cores extracted from deteriorated structures and on rocks of similar lithologic facies, sampled in different points of the island (especially in South East of Quartier d'Orléans).

Magmatic rocks present in variable quantities in concrete, contain phenocryst of sodium-calcium feldspars (plagioclase) and pyroxenes of augite type often ouralitized (transformation in amphiboles). The phenocryst, included in a granular, microgranular or microlitic groundmass, are plagioclases, quartz and pyroxenes. In some cases texture can go from microgranular to porphyritic granular in the same fragment. Following this texture, rocks can be classified among the diorites, quartz microdiorites or andesites basalts. Locally, enrichment in calcite, quartz, epidotes, garnets and chlorites corresponds to endomorphic or metasomatic transformations.

Multicoloured or green silicon-calcium rocks which are in high quantity in the most deteriorated concretes, correspond to interstratified tuffs partly transformed in contact with magmatic rocks. As the case may be, they are constituted by crystalline to sparry calcite or by siliceous dyscrystalline groundmass including broken crystals essentially of feldspar. The calcitic facies correspond to more carbonated levels alternating with pyroclastic products. Some fragments show the contact between tuffaceous levels and quartz microdiorites.

Transformations to metamorphism or to metasomatic phenomena leads on one hand to a network of string filled with clays associated with sparry calcite or euhedral quartz and on the other hand to the presence of secondary minerals often in high amount. Clays, which sometimes substitute the siliceous or carbonate groundmass of the tuffs, correspond to clayey phyllosilicates 2:1 (Te-Oc-Te) trioctahedral with a variable equidistance of stevensite type $Mg_3 [Si_4O_{10}] (OH)_2$. Globally, in the mineral paragenesis induced by physico-chemical transformations, silicates or various non usual calcium and magnesium aluminosilicates are prevailing. Except stevensite, euhedral quartz and calcite, the following minerals can be identified: calcic garnets of grossularite type $(Ca_3Al_2 [SiO_2]_3)$ or hydrogrossular, epidotes (epidote *s.str.* and clinozoisite), prehnite $Ca_2Al_2 [Si_2O_{10}] (OH)_2$, wollastonite $CaSiO_3$, diopside (Ca, Mg $[Si_2O_6]$) and, in particular instances, vesuvianite (Fig. 3).

From the petrographic point of view these rocks can be classified among tactites or hornfels.

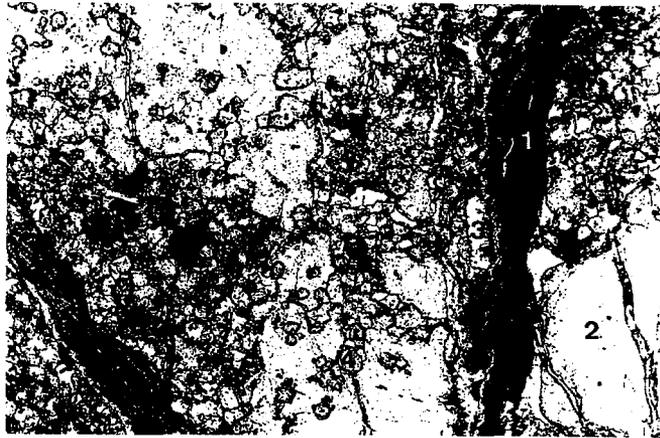


Fig. 3 Petrographic microscope, magnification $\times 53$, PPL, tactite, 1 = stevensite, 2 = prehnite, 3 = calcite, 4 = grossular, 5 = diopside

CHARACTERIZATION OF AAR PRODUCTS

Products observed at the tip of the pop-outs and altered aggregates from the core of concrete deteriorated by bulk cracking clearly have, in both cases, a weak cohesion and a grey or greenish brown colour reminding the metamorphic interstratified tuffs. The different analysis confirm this observation by showing the presence of metamorphism silicates (garnets, wollastonite) associated to quartz, calcite and clayey minerals.

Despite the aggregates involved in both mechanisms of AAR are similar and correspond essentially to contact facies between magmatic rocks and interstratified tuffs, the analysis show great differences in the reaction products.

Products taken from apex of the pop-outs have a particularly low compactness. They are constituted by a clayish groundmass including residual non altered minerals such as quartz, calcite, garnets and wollastonite. Clayey minerals differ from the original one and correspond as the case may be, to swelling irregular interstratified minerals and/or to 2:1 phyllites with an equidistance around 10 Å. Residual minerals are associated to gels of very low viscosity filling the porosity of the altered aggregate or in contact with it. The EDS analysis of these gels show that they essentially have a siliceous and alkaline composition with a high $\text{SiO}_2/(\text{Na}, \text{K}_2\text{O})$ molar ratio of about 8 to 11.

In the case of bulk reactions, the appearance and composition of AAR products depend clearly on the initial mineralogical composition of the aggregate. However, in general, the alteration process goes on by concentric and progressive steps from the periphery to the center. Residual products of AAR contain calcite, quartz and garnets associated to clayey minerals partly exfoliated corresponding to irregular interstratified swelling minerals.

As in the case of pop-outs, the disappearance of the prehnite seems to show that this mineral is destroyed by AAR. On the contrary, while wollastonite does not seem to react in physico-chemical conditions leading to formation of pop-outs, it appears clearly implied in reaction within the concrete. This alteration increases from the core to the periphery of the mineral. As published (P. Réry *et al.* 1992), wollastonite is associated to silicon calcic alkaline gels. At high magnification, the altered surface of the wollastonite crystals, are covered by clusters of lamellar crystals containing silica, calcium and slightly alkalis (Fig. 4). Their elementary composition when compared to wollastonite shows an enrichment in alkali to the detriment of calcium.

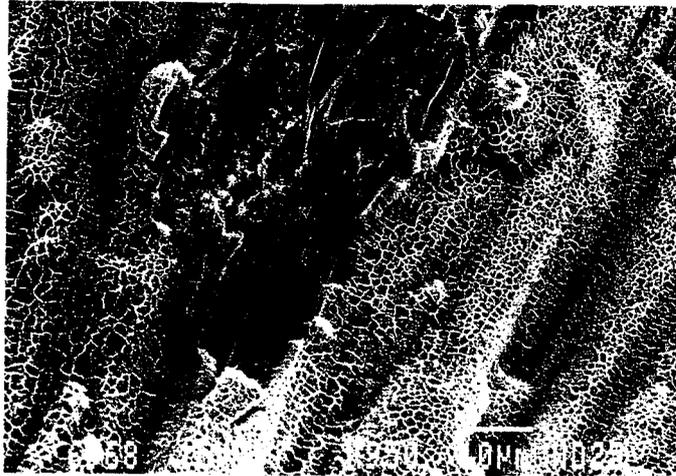


Fig. 4 SEM, crystal of wolastonite embeded in AAR products

Residual products of bulk reaction are accompanied by gels in the cement paste or at the interfacial zone between cement paste and aggregates. The appearance of the gels varies from smooth gels to lumpy gels. Their chemical composition also varies in relation to their distance from the aggregate. They are mainly alkali-silica gels in zones close to reactive aggregate but they show a progressive enrichment in calcium when coming in contact with the cement paste. It is characterized by $\text{SiO}_2/(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO})$ molecular ratios varying most often from 1.5 to 3. In some cases, they can contain a significant amount of magnesium.

MECHANISMS

Mechanisms of AAR are usually controlled by the presence of potentially reactive minerals in the aggregates, and by environmental conditions which, in the present case, is characterized by relatively high relative humidity and temperature and by a high content of alkaline oxides.

The main characteristics of aggregates involved in the different mechanisms of AAR is the occurrence of prehnite, wollastonite and in some cases, forms of subamorphous silica. The nature of the AAR residual products and the most often low quantities of badly crystallized silica show that in the present case, AAR are essentially alkali-silicate type.

Generally speaking, the stability conditions of the silicates are in direct relationship with their chemical composition and crystalline structure. The nature of the neogenic products and the kinetics reaction both depend on these characteristics.

From this point of view, stevensite $\text{Mg}_3[\text{Si}_4\text{O}_{10}](\text{OH})_2$, a 2:1 (Te-Oc-Te) clayey trioctaedric phyllosilicate having variable equidistance, seems to be the most easily alterable silicate, especially because of the presence of interfoliar layers which can absorb alkaline solutions.

Prehnite is a nesosilicate (tetrahedron $[\text{SiO}_4]^{4-}$ linked to each other by cations) of formula $\text{Ca}_2\text{Al}_2[\text{Si}_3\text{O}_{10}](\text{OH})_2$, belonging to the orthorhombic system. Its misunderstood crystalline structure, close to brittle micas, is formed by piling up of brittle lamellae (Deer *et al.*, 1966) Its properties also draws it close to zeolites (A. Foucault *et al.* 1988). Such a structure also probably leads to relatively high reactivity in alkaline solutions.

Wollastonite $\text{Ca}(\text{SiO}_3)$ belongs to the triclinic system. It is a pyroxenoid (inosilicate) constituted by chains of silica tetrahedrons associated to chains of calcium atoms in deformed octahedra. The fusion of two chains (i.e. by alteration) does not lead to occurrence of an amphibole as in pyroxenes, but to the hydrated calcium silicate xonotlite $(\text{Ca}_6(\text{Si}_6\text{O}_{17})(\text{OH})_2)$ (Deer *et al.*, 1966).

Cristallographic and chemical characteristics of these sensitive minerals allow to propose mechanisms in order to explain their contribution to the observed AAR.

By analogy with weathering of the 2:1 phyllosilicates (Pedro *et al.*, 1979), the strongly basic conditions and the salts content of concrete can be close to natural conditions leading to transformations by partial hydrolysis, salinolysis and alkanolysis.

Concerning the stevensite, in a first time, alkaline solutions (Na^+ , K^+ , Ca^{++} , OH^-) can penetrate quickly into the interfoliar structure of the mineral, leading to expansion of the crystal lattice.

This process leads on one hand to rock destructuring and swelling and on the other hand allows the alkaline solution to come in contact with the silicates (prehnite, wollastonite) and the less abundant subamorphous silica.

Reaction mechanisms between alkaline solutions and badly crystallized silica have been studied by many authors (Dent Glasser *et al.*, 1981, Poole, 1992...). They can be summarized by a neutralization of acid silanols radicals Si-OH by alkaline ions and, in a second time, by an attack of the siloxanes bridges Si-O-Si by the OH^- ions. This reaction leads to destruction of the mineral and formation of a polymerized alkali-silica gel.

The silicates alteration could take place following similar mechanisms. According to B. Madé (Madé, 1994), dissolution of silicates in rocks is controlled by the formation of bonds between water and the siloxane and silanols groups and by hydrolysis reactions at the minerals surface. These reactions leads to formation of silanols groups due to breaking the Si-O of the silicated lattice. In addition, because of a pH higher than 9 in the interstitial solution, the kinetics reaction is accelerated and the released silica is in the form of ionized silicic acid $(\text{SiO}_3)^{2-}$. The decrease of pH by consumption of OH^- ions and neutralization of the negative charges by alkaline ions favor polymerization of silica and formation of a silicon-alkaline gels.

In these conditions the three silicates: stevensite, prehnite and, to a lesser extent, wollastonite, can transform and lead to the formation of silicon-alkaline gels.

In the case of stevensite, the tetrahedra layers in close contact with alkaline solutions can be attacked rapidly leading to the formation of silicon-alkaline gels and irregular interstratified clayey minerals and if further reaction is possible, to the formation of new clayey 2:1 phyllosilicates (Millot *et al.*, 1965, Tardy, 1970). It must be noted that in more confined conditions, formation in situ of aluminosilicates, zeolites or feldspathoid type minerals, is possible (Pedro *et al.*, 1979). Such mineral species have been reported (Batic and al. 1992) as products of AAR from montmorillonites.

The formation of clayey 2:1 phyllosilicates, partly well crystallized (irregular interstratifieds), also appears to come from reactions with prehnite. The crystalline structure and the chemical composition of wollastonite, seem mainly to lead to silicon calcic alkaline gels. However, the lamellar morphology, allow the presence of xonotlite $(\text{Ca}_6(\text{Si}_6\text{O}_{17})(\text{OH})_2)$. In the present case, this hydroxylated mineral could correspond to a natural phase associated to the wollastonite or result from its alteration. Whatever the case, due to its structure and its hydroxylated composition, xonotlite is probably more sensitive to alkaline solutions than wollastonite.

Although aggregates involved in pop-outs formation and bulk cracking are of similar mineralogical nature, it seems that the reactional mechanisms differs according to the local physico-chemical conditions of each AAR: alkali concentration, relative humidity, compactness and mechanical strengths of cement paste with respect to its capacity to withstand swelling pressures.

In the case of pop-outs, the rapid kinetics reaction can be explained by expansion of stevensite due to penetration of the alkaline solution in interlayer position. Moreover, the expansion is made easier by a weaker opposition to swelling forces than in the concrete core. Furthermore, gels formed by attack of silica and silicates such as stevensite and prehnite are mainly siliceous alkaline gel with an increased $\text{SiO}_2/\text{K}_2\text{O}$ molar ratio. The composition of these gels of low viscosity and having a high water content places them probably quite far from the pessimum conditions and gives them a weak expansive capacity (Hornain, 1994).

In the case of bulk cracking, confinement leads to stronger resistance to swelling and limits the effect of the relatively weak expansion stress of clays, promoting alkali-silica and alkali-silicates reactions. The latter, especially in the case of wollastonite, could be made easier by enrichment and confinement of the alkaline solution in associated phyllites. The reaction has a slower kinetics and leads to the formation in a first time of a silicon alkaline colloidal solution (sol) that coagulates and transforms into gels in the presence Ca^{2+} ions. The formation of viscous silicon calcic alkaline gels, of weak molar ratio $\text{SiO}_2/(\text{K}_2\text{O}+\text{CaO})$, would develop swelling pressure high enough to induce cracking of concrete. However, the question is still open whether the expansion stress is due to gel in the course of its "formation" (something like "pressure of crystallization") or its "transformation" (calcium fixation and coagulation of a colloidal unstable suspension of silica (Wen 1989) in the form of a hydrophylic gel likely to generate osmotic pressures). Pop-outs formation might represent a first stage of ASR. The products of low viscosity associated to pop-outs formation might correspond to nascent gels which become more viscous when coming in contact with the calcium of the cement paste. Only the rapid kinetics reaction of specific aggregates allows the presence of such fluid siliceous gels which are quickly transformed in confined conditions. This scenario seems to be confirmed by EDS analysis which show the siliceous nature of the gels close to the reactive aggregates and the progressive increase of their calcium content towards the cement paste.

CONCLUSIONS

The present study confirms silicates reactivity, especially of phyllosilicates of smectites type (i.e. stevensite) in environmental conditions favourable to AAR (temperature, humidity, high alkali content, marine environment).

These reactive aggregates, close to the concrete surface, give rise to pop-outs formation. The same aggregates can lead to characteristic cracking of bulk AAR.

The two forms of alkali-reaction do not coexist systematically. Especially, pop-outs can be present alone. This phenomenon can be explained by local physico-chemical variations in concrete: alkali concentration, water content, capacity to withstand swelling forces.... These variations induce different reaction mechanisms and kinetics.

The rapid formation of pop-outs is in relation to the presence of reactive aggregates close to the concrete surface, high relative humidity and enrichment in alkali as a result of the migration of K^+ , Na^+ ions. The reaction would be controlled by smectites exfoliation due to alkaline solutions penetration in interfoliar position. It leads to the formation of a fluid mainly silico-alkaline gel.

In the case of bulk cracking, the major role of swelling phyllites would be the enrichment and the local confinement of alkaline solutions which would favor alkali-silica and alkali-silicates reactions also including minerals such wollastonite.

These reactions lead to silico-calco-alkaline gels, the formation of which induces concrete cracking. In any case, appearance of bulk cracking is also in relationship with the quantities of potentially reactive minerals in aggregates.

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