INHIBITION OF ALKALI-AGGREGATE REACTION BY NON POZZOLANIC TREATMENT

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Some of results relating to the use of non pozzolanic materials to inhibit alkali-silica-reaction are already reported. These admixtures (Crown Ethers, lithium compounds etc.) are added to mortars or concretes to inhibit the expansion. The inhibiting effects are preventive and not curative.
The present paper deals with trials to inhibit the alkali-silica reaction in view of curative treatment. The inhibition effect was appreciated in terms of expansion and modification of gels structure.

INTRODUCTION

Damage to reinforced concrete structures caused by alkali-aggregate reaction, principally alkali-silica reaction, is being encountered with increasing frequency and giving rise to considerable concern in France. A large number of studies on the prevention and reduction of the harmful effects of this reaction are on the agenda and have been the subject of several research projects justified by the benefits which they could produce.

With regard to remedial treatments, which are very often unsuccessful, the most frequently studied techniques concentrate on passive reduction of the moisture content of concretes (water-repellent coatings, surface treatments, etc.) or the structural reconstitution of concretes (treatment of cracks with resins). Few projects aim at blocking development of the reaction by acting on the alkali content parameter.

Other treatments, usually chemical treatments appraised by laboratory trials on test pieces, have proved to be effective (1) (2) (3) (4) (5), but these treatments are preventive in nature since the reaction inhibiting agents have been added to the mixing water.

The following can be quoted as an indication :

- chelating molecules: * B - cyclodextrine
* ether-crowns
* monohydrate calcium phosphate

- other molecules: * sodium fluorosilicate
* lithium salts
* alkoxysilane alkyl
* barium hydroxide

In certain cases, these products have been applied to cracked test pieces by means of impregnation, and the latter have exhibited reduced expansion in comparison with test pieces not treated by impregnation (3).

The object of this work is firstly to demonstrate the chelating power of a water-miscible organic molecule in any proportion in a basic medium of the pore solution type, and secondly to apply it to a test piece exhibiting cracking as a result of alkali-aggregate reaction, in order to correlate the microstructure of the gels in the treated test pieces and the expansion thereof.

Although there is no standard test to demonstrate the inhibition of expansion by impregnation with a chelating product, we selected the ASTM C441 test for two reasons:

- it is a rapid test which provides an idea of the potential efficiency of remedial treatment by impregnation.

- this test, adopted in publications (3) for this type of treatment, has produced satisfactory results.

CHELATION OF ALKALIS IN BASIC MEDIUM

We were interested in the chelation of K+ in aqueous medium KOH 0.6 mol/l (ionic strength of the same order as that of the pore solutions) and in a 50/50 by volume water/methanol medium, using an organic molecule miscible with these two solvents. This molecule will be referred to as C.

Equipment and solutions used

The concentration of free K+ was determined by potientometry using a selective electrode with K+ ions, a reference electrode (HgO/Hg) and an ionoprocessor.

The ionic strength was maintained at constant level by adding an neutral electrolyte.

It should be noted that chelate C does not change the ionic strength of the medium.

Results

In water

(KOH 0.6 mol/l + C 0.6 mol/l)

The concentration of free K+ = 0.07 mol/l which gives a chelation rate of 88%.

In water + methanol medium

(KOH 0.6 mol/l + C 0.6 mol/l)

The concentration of free K+ = 0.014 mol/l which gives a chelation rate of 98%.

From these results, it is possible to determine the constants of stability of the chelate formed in the two media. By applying the law of action of mass, the constant of stability of the reaction

$$K + C \longrightarrow CK \quad \text{is} \quad K' = \frac{(K)\ (C)}{(CK)}$$

(K) concentration of K
(C) concentration of Chelate C
(CK) concentration of Complex CK

K' is an apparent constant because the constant of equilibrium involves the activities and not the concentrations.

- in water + methanol medium

free K+ = 0.014 mol/l

$$\begin{array}{llll} & K\ + & C \longrightarrow & CK \\ \text{at time } t = 0 & 0.6 & 0.6 & 0 \\ \text{at time } t\ \text{eq} & 0.6-x & 0.6-x & x \end{array}$$

The concentration of K at equilibrium is (K) = 0.014 mol/l hence 0.6 - x = 0.014 ---> x = 0.586 mol/l

$$K1' = \frac{0.014 \times 0.014}{0.586} = 3.34\ 10^{-4}$$

hence pK1' = -log K1' = 3.47

- in water

The same calculation gives pK2' = 2.03

The thermodynamic constants in a water/methanol medium (thus involving the coefficients of activity of the cations) are shown in table 1 :

TABLE 1 : Thermodynamic constants of stability chelate C/cations in water/methanol medium

cation	Li+	Na+	K+	Rb+	Cs+	Mg++	Sr++	Ba++
LogKs	2.0	2.2	2.2	2.0	2.0	2.0	2.1	2.7

Ks is the constant of stability defined by the relation

$$Ks = \frac{a(k)\ a(c)}{a\ (ck)}$$

with : Ks : thermodynamic constant stability
a : activity

Although the values are different (apparent constant involving the concentrations and thermodynamic constant involving the activities), our results confirm the considerable chelating power of chelate C.

Although the rate of chelation in water is lower than the rate of chelation in the water plus methanol medium, the free K+ content in the aqueous solution is low.

EFFECT OF CHELATION ON ALKALI-AGGREGATE REACTION

Effect of chelating treatment on microstructure of gels.

Tests for chelation of K+ in a basic aqueous medium, using chelate C, demonstrate that it is possible to trap 88% of the K+ in solution.

We have attempted to make use of this chelation property by treating cracked test pieces (4 x 4 x 16 cm) defined for test ASTM C441 (pyrex + OPC cement Na_2O eq = 1%), in which silicocalcopotassic gels characteristic of alkali-aggregate reaction have formed.

The curve shown in Figure 1 represents the variation in expansion in the course of time for up to 14 days of testing.

After 14 days of testing, four test pieces were dried in air for 24 hours.

Two test pieces were immersed in water at 20 degrees C and the other two were immersed in the water + chelate C medium at 20 degrees C for three days.

A comparative microstructure study carried out on the samples immersed in each medium showed that :

* In the case of the test piece immersed in water:

The mortar contained abundant silicocalcopotassic alkali-aggregate reaction gels, usually smooth and less frequently with variable microtextures :

- more or less swollen
- partially or totally crystallised
- botryoidal

(See Photograph 1 - Figure 2)

* In the case of the test piece immersed in water + chelate C

The gels retained the same microtexture (photograph 2) but no longer contained potassium and, in some cases, were impoverished in calcium (see spectra, Figure 3)

The presence of new crystallisations covering the whole of the hydrated cement paste, and sometimes, locally, the alkali-aggregate reaction gels, was noted.

These crystals with variable facies contained a large quantity of calcium always associated with much smaller quantities of silicon.

This microstructure study demonstrates that it is possible to chelate the alkalis of gels.

In order to correlate the microstructure changes of the gels resulting from impregnation at 20 degrees C by chelating agent C, with the expansion phenomenon, we carried out an ASTM C441 test (temperature 20 degrees C) using the same cement, and pyrex.

Effect of impregnation with chelate C on expansion

We mixed six mortar test pieces (4 x 4 x 16 cm) consisting of pyrex + OPC cement, Na_2O eq = 1%.

After being removed from their moulds, these test pieces were dried and then some of them were immersed in water and others in a 50/50 by volume solution of water/chelate C (3 test pieces). This operation was repeated after one week of testing. The test was carried out at 20 degrees C, 100% HR.
The progress of expansion in the course of time, for a period of 14 days, is illustrated in Figure 3.

We observed a reduced expansion in the test pieces impregnated with chelating agent C as compared with the non-impregnated test pieces.

This reduction in expansion can be linked to the change in the microstructure of the gels (see paragraph III.1) where we see firstly gels with no K alkali, and secondly the appearance of new crystallisations containing calcium and silicon.

DISCUSSION

The study of chelation in basic medium KOH, using chelate C, demonstrated that it was possible to trap ion K+ by means of a water-miscible organic molecule, producing greater chelation in a water/methanol medium than in water. This is explained by the higher solvation capacity of water compared with a water/methanol medium, since the constant of stability of the chelate is higher in this medium.

The microstructure study demonstrated that silicocalcopotassic gels impregnated with chelate C are deprived of potassium; this happens as if the following reaction (in outline) were present:

(CSKH) + (C) --> (CSH) + (CK)
(C): chelate (CSKH) : Gel silicocalcopotassic
(CSH) : Gel without K and/or crystals calco-silisic
(CK) : complex

This result confirms that the SiO...Na bond within the gels is not a covalent bond. These are adsorbed cations.
This result confirms the exchange property of gel cations, such as UO22+ uranyl ions (works by K. NATESAIYER and K.C. HOVER (6) and S. GUEDON (7)), or Cu++ ions (8).

Furthermore, it has been demonstrated that the adsorption of calcium ions is greater than that of monovalent cations such as Na+ and K+, and this is linked to electrostatic bonding energy: higher for the Ca-O bond than for the Na-O bond (9).

Trapping cations by means of a chelating molecule results in reduced expansion. This result does not contradict the mechanisms put forward by H. WANG, GILLOT (10) and CHATTERJI (11), based on Ca++/Na+, K+ exchange phenomena on the silanol sites of gels, and on the cation diffusion process.

CONCLUSION

This study has shown that it is possible to inhibit alkali-aggregate reaction by chelating the cations adsorbed by the Si-O- groups of gels.

Further tests are in hand on natural aggregates containing reactive material. The reduction in expansion is not great, probably because of the miscibility of chelate C and water. Treatment with chelate C in an organic medium should reduce expansion more than this treatment, especially since the structure of chelate C means that it may feature phase transfer reaction; in other words, the gel will become soluble in an organic solvent not miscible with water. In addition, this study has made it possible to demonstrate the important role of alkalis in the alkali-aggregate reaction mechanisms.

Further studies are in course and will be included in this report.

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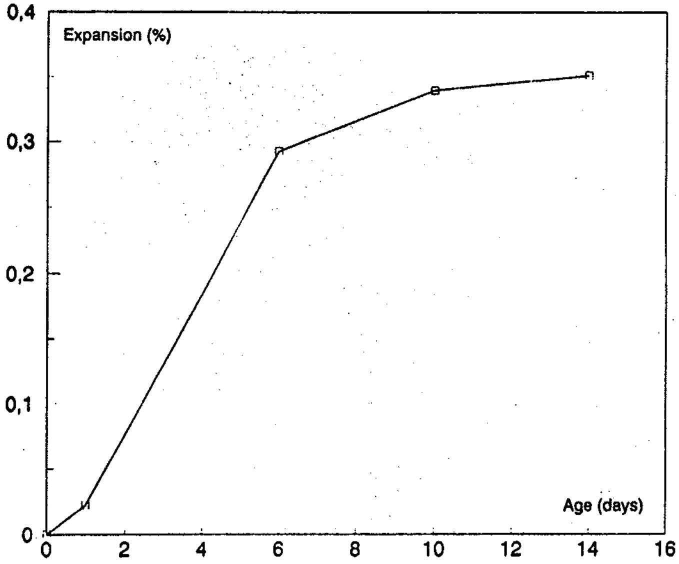
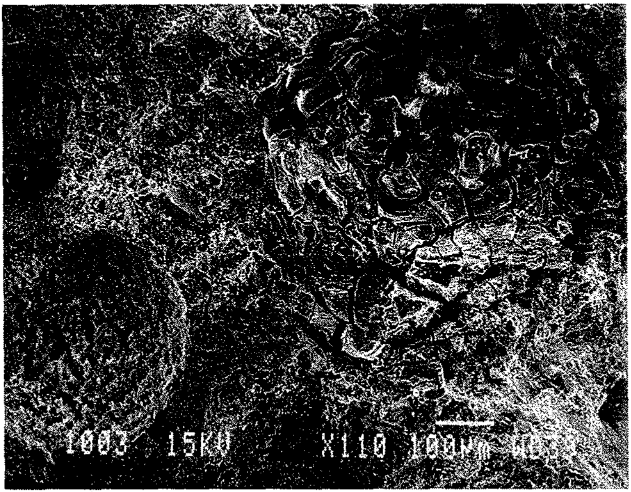


FIGURE 1 : TEST ASTM C 441 (PYREX + CEMENT OPC Na_2O eq = 1 %)



PHOTOGRAPH 1
Untreated sample immersed in water

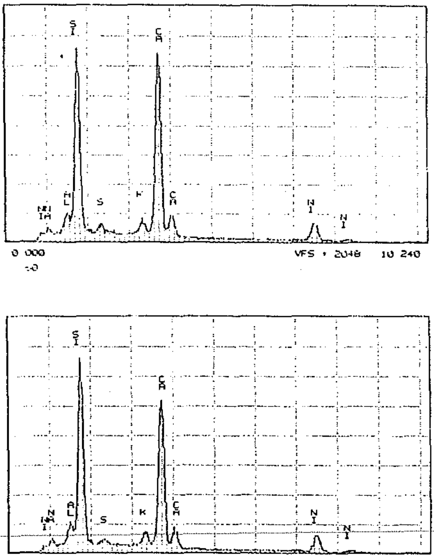


FIG N° 2 : Typical sample (untreated)
EDS analysis of alkali-aggregate reaction gels

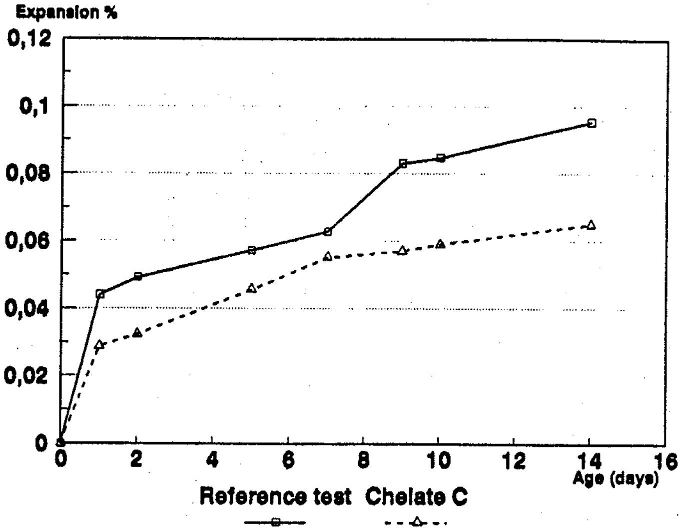


FIGURE 3 : Type test ASTM C 441 (tp) 20°C) Imprégnation 24 h (water + chelate C 50/50 v/v) at t = 0 and T = 7 days

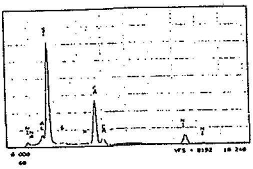
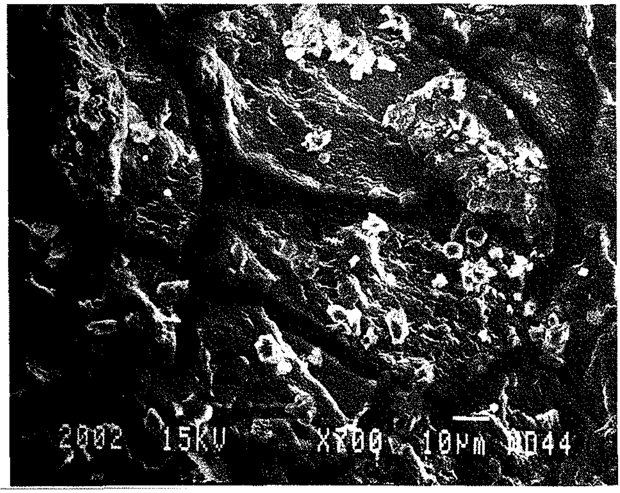


PHOTO 2 : Microstructure of gels in the treated sample : mooth gels covered locally with particles containing calcium and silicon



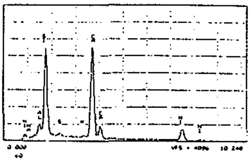


FIGURE 4 : EDS (spectrum) of gels in the treated sample

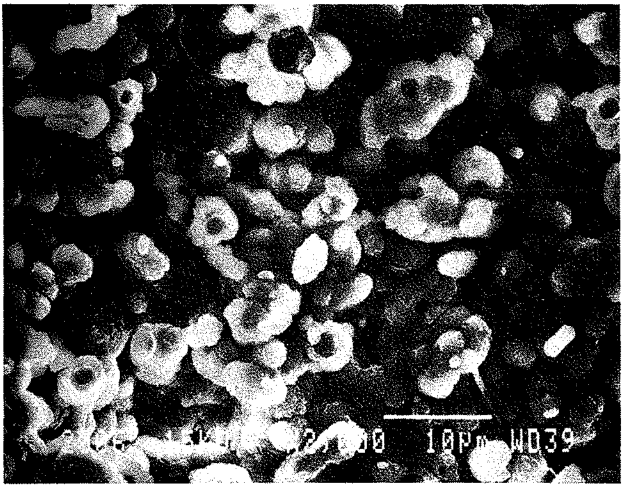
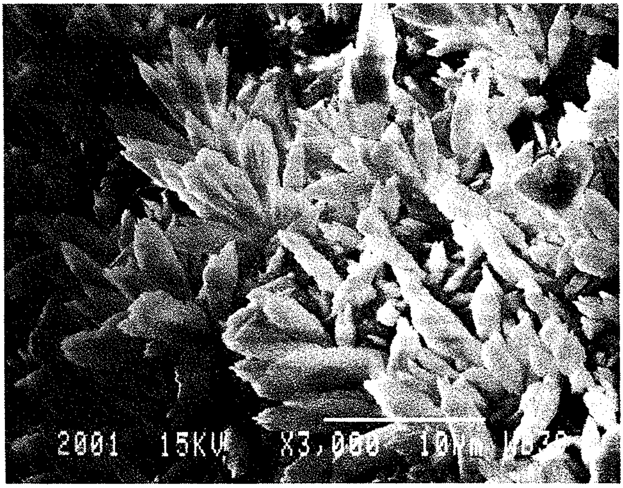


PHOTO 3 : Crystals covering the whole of the cement paste. Note the variable facies of the crystals.



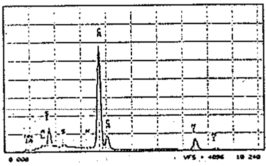


FIGURE 5 : EDS (spectrum) of the crystals in the photo 3 above