STUDY OF Ca-Si GELS, PRODUCT OF ALKALI-SILICA REACTION.

Lombardi, J *, Perruchot, A*, Massard, P * and Larive, C* *

* Laboratoire de Géochimie des Roches Sédimentaires, Université Paris-Sud, Bât. 504, U.R.A. 723 du C.N.R.S., 91405 ORSAY Cedex and GEO 1994-1996 Network.
**Laboratoire Central des Ponts et Chaussées, Division Ouvrages d'Art, Section Durabilité des Ouvrages d'Art 58 bd Lefebvre 75732 PARIS Cedex 15.

ABSTRACT : A comparative study has been made of Ca-Si gels product of alkali silica reaction in hydraulic concrete and synthetic gels.

The morphological characteristics and chemical compositions of natural Ca-Si gels were determined from samples taken from test cylinders (16 x 32 cm), tested for 28 days at 60°C and 100% H.R.. Synthetic gels with known CaO/SiO_2 ratios were placed under the same test conditions.

A comparison between the morphological and chemical characteristics of the gels was carried out using SEM.

The main results are :

- after testing both types of gel show that their CaO/SiO_2 values have characteristic average values of 0.43;
- both types of gel show the same variation of their SiO_2 and CaO contents ;
- under similar conditions, natural and synthetic gels present the same morphological characteristics ;
- Na and K do not seem to be incorporated into the structure of natural and synthetic gels.

The study of physico-chemical properties of synthetic gels facilitates the understanding of the formation processes of gels product of alkali-aggregate reaction.

Keywords : Alkali-aggregate reaction, Alkali-silica reaction, chemistry of gels, synthetic gels

INTRODUCTION

First identified in the United States (Stanton 1940), alkali-aggregate reaction (AAR) appears , more and more, to be the cause of functional disorders, swellings and crackings, observed in structures. The chemical and physical mechanisms of these reactions remain the purpose of many studies and controversies, and it is generally assumed that these disorders are attributable to Ca-Si gels produced by those AAR. The growth of these "pathogenic" gels in the porous space of concrete induces expansive pressions that can reach 5 MPa (Chongxi 1986). They are identified as the cause of the swellings and the crackings observed. These disorders can strongly alter the mechanical characteristics of structures such as bridges or dams.

The alkali-aggregate reactions have been classified into three types : the alkali-silica, alkali-silicate and alkali-carbonate reactions. Several factors contribute to their formation. They are, essentially, the nature of the aggregate, the content in alkalis of the cement, the humidity of the environment and the temperature. However, the main controlling factor, remains the cement-aggregate-pore solution system. In all these reactions, the role played by the silica appears decisive, even in the case of alkali-carbonate reactions.

The product of alkali-silica reactions is a hydrated gel containing silica, calcium and alkalis. Those three constituents are present in variable proportions : SiO_2 from 28 to 86%, CaO from 0.1 to 60%, K_2O from 0.4 to 19% and Na_2O from 0 to 20%, (Arsberetning 1969, Baronio 1983, Brouxel &Valiere. 1992, Buck & Mather. 1969, 1978, Diamond 1983, French 1976, Hester & Smith. 1956, Idorn 1961, McConnell *et al.* 1947, Oberholster 1983, Poole 1976, Regourd *et al.* 1981, Stanton 1942, Thaulow & Knudsen. 1975). However, the two most important constituents are SiO_2 and CaO, of which the ratio CaO/SiO_2, noted C/S, in practice defines the composition. In fact, this composition gives rise to the physical and chemical properties of this gel as adsorption and swelling (Dent-Glasser & Kataoka. 1981, Diamond *et al.* 1981, Lea 1973, Powers & Steinour. 1955, Verbeck & Gramlich. 1956, Vivian 1983).

The aim of this study is to define the morphology and the chemical composition of natural gels taken from cores of concrete affected by the AAR. The synthesis of characteristic gels, of which the chemical composition is as close as possible to the natural gels, is used to follow experimentally their morphological and chemical evolutions under the standard conditions of AAR development. The results obtained from synthetic and natural gels will be compared.

MATERIALS AND METHODS

Natural gels

The morphological and chemical analysis of gels requires a representative, homogeneous quantity of product. That is why we chose to place a range of test cylinders of concrete under the conditions favouring the rapid development of the alkali-aggregate reaction.

The concrete was made from the following constituents : cement CPA 55, limestone aggregate (Spratt), classified as alkali reagent from P 18-589 French norm and fluvial sand (silica and limestone). The characteristics of the mix are given in Table 1.

The test cylinders of concrete, 16 cm in diameter, 32 cm in height, were tested for 21 days at 60°C and under 100% relative humidity

Table 1 :Composition and W/C ratio of concrete used for test cylinders.

Constituents	Cement	Water	Sand (Seine)	Aggregate (Spratt)	W/C
weight (Kg)	12.3	6.15	20	34.5	0.5
Percentage (%)	16.86	8.43	27.42	47.29	

At the conclusion of the test the gels were isolated after fragmentation of the concrete cylinders using a hydraulic press. Their morphology was studied at several levels, first with a binocular microscope, then -after carbon plating-with a SEM . The chemical composition of the gel was determined by point count analysis (around 600) by spectrometry X with energy scattering (EDS, LINK AN 10000 coupled with a SEM PHILIPS 505). The results, normalised at 100%, are given in percent of oxides using the program LINK ZAF 4 PB, adapted to the analysis of roughened areas.

Synthetic gels

We chose to prepare the Si-Ca gels with C/S ratios of 0.5 and 1, which appeared to be very close to the C/S value of the natural gels.

The technique used (Perruchot & Delbove. 1982a,b, 1991) enables sufficient quantities of gels with controlled compositions to be produced.

- C/S = 1

To x ml of a solution of SiO_2Na_2O 0.1M we add x ml of a solution of $CaCl_2$ 0.1M. A gel, with a composition of SiO_2,CaO,nH_2O precipitates quickly in accordance with the following balanced reaction :

$$SiO_2Na_2O + CaCl_2 + nH_2O \rightarrow [SiO_2,CaO,nH_2O]_{gel} + 2\ NaCl \quad [1]$$

- C/S = 0.5

To x ml of a solution of SiO_2Na_2O 0.1M, add x/2 ml of a solution of $CaCl_2$ 0.1M and x/10 ml of a solution of HCl 1M. A gel, with composition of $2SiO_2,CaO,nH_2O$, precipitates in accordance with the following balanced reaction :

$$2SiO_2Na_2O + CaCl_2 + 2HCl + (n-1)H_2O \rightarrow [2SiO_2,CaO,nH_2O]_{gel} + 4\ NaCl \quad [2]$$

In order to recover gels (reactions 1 and 2) without NaCl, they are washed in a solution of KOH 0.2 M, with a pH of 13.3 which is very close to the pH of interstitial solution in concrete (Longuet *et al.* 1974). They are then separated from the washing solution by centrifugation. This operation has a double justification. On the one hand, the pH of the gel-solution systems are 13 for C/S =1 and 11.6 for C/S = 0.5, and therefore a simple washing with distilled water (pH = 5.7) will dissolve the gels ; on the other hand, the washing with KOH offers the opportunity to follow the behaviour of the potassium ions in synthetic gels, and to observe whether or not they can be integrated into the structure of gels.

The morphological and chemical behaviour of the synthetic gels have been experimentally followed under similar conditions to those in which gels develop in concrete test cylinders. One cm^3 of each synthetic washed gel was spread on 4 cm^2 of an inert silica-aluminous material, whose porosity was very close to the porosity of concrete. During 28 days, these samples were kept at 60°C and 100% relative humidity.

RESULTS

Natural gels

Morphology

Observation of the concrete cylinders, visually and with a binocular microscope, shows that the gels grow preferentially into the coarse porosity of concrete (Fig. 3a,3b).

The presence of gels at the contact of the aggregates or in the cement paste could not be observed directly. However, with the uranyl acetate test (Guedon & Martineau. 1991, Guedon *et al.* 1992, Natesaiyer & Hover. 1988) we have observed these types of gels. The real distribution and the amount of all gels could not be observed on the concrete cylinders studied but only the gels present in the cavities, which have been isolated and analysed.

The strongly hydrated gels observed in the concrete cylinders are characterized by a milky white homogeneous colour. In the finer cavities the gel occupies all the available space (Fig. 3a). On the other hand, large cavities are only partially filled (Fig. 3b).

The drying of the gels under atmospheric conditions is quick and leads to characteristic facies. In the fine cavities the gels form as pseudo spherical units that can easily sampled.(Fig. 3a) ; in coarser cavities the gel presents the typical desiccation phenomena (Fig. 3b).

Obviously, the morphological aspect of the gels is connected to the observation scale. At a magnification of 2,400, (Fig. 3c), the gel exhibits a very irregular aspect with a spongy texture.

Chemical composition

Nearly 600 point analyses have been effected on the gels present in the cavities. These analyses show that the main constituents of the gels are the four oxides

SiO_2, CaO, K_2O and Na_2O. The contents of those oxides change from 3.20% to 85.40% for SiO_2, from 1.45% to 68.45% for CaO, from 1.10% to 33.70% for K_2O and from 0% to 7.60% for Na_2O. We observe these variations in all the analysed cavities, and, at a higher magnification, within the units bounded by desiccation cracking.

The variation of the C/S ratio, between 0.05 and 13, confirms that the gels at this scale of observation have several compositions. The graphic representation of the SiO_2 contents according to the CaO contents (Fig. 1) distinguishes three principal fields of composition.

Within the first field, 23% of the analyses, the percentage of SiO_2 changes between 55 and 70% and the percentage of CaO between 10 and 18%.
Within the second field, which includes 63% of the analyses, the percentage of SiO_2 changes between 45 and 65%, and the percentage of CaO between 15 and 30%. Finally, within the third field, 14% of the analyses, SiO_2 changes between 5 and 40% while CaO changes between 30 and 90%.
From these results we can determine a correlation between these two oxides. The coefficient of variation is 0.93, a very good value taking to account the large number of analyses. The average of the C/S ratio of the gels, is 0.43 which can be considered characteristic (Fig. 2) .

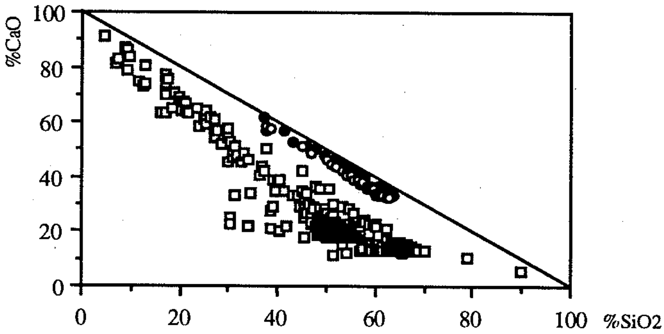

Fig. 1 Correlation between CaO and SiO_2 contents for natural and synthetic gels (Correlation coefficient, R = 0.93). □ : natural gels; ○ : synthetic gels, C/S = 0.5 ; ● : synthetic gels, C/S = 1.

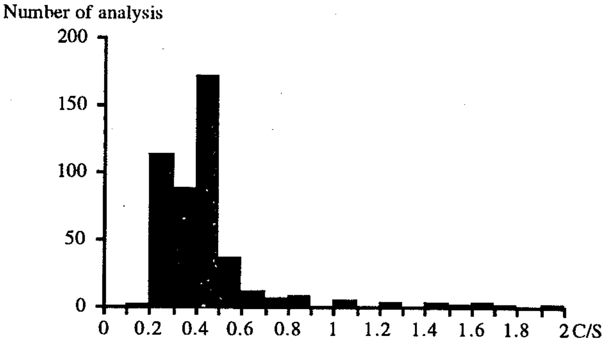

Fig. 2 Histogram of C/S ratio for natural gels.

The graphic representation of the SiO_2 contents, according to the K_2O contents, provides a correlation coefficient of 0.35. By comparison with the precedent coefficient these two oxides have a low correlation. Na_2O does not correlate with the other oxides.

Synthetic gels

Morphology

As for natural gels, synthetic gels are characterized by their milky white homogeneous color. Their dehydration, also very rapid, leads to the same morphology as natural gels. We find, at all magnifications, the same characteristics : a net of desiccation cracks and, at high magnification, surfaces with a spongy texture (Fig. 3d).

Chemical composition

The total analyses of gels recovered after washing by KOH 0.2 M on the one hand show that the sodium is totally eliminated and, on the other hand, that up to 4% of potassium is present.
The C/S values determinated from these total analyses are respectively 0.48 and 1.06, in agreement with the equations 1 and 2.
The concentrations of Na_2O measured in the last washing solutions of the two types of gel are close to 1 mg/l ; this fits with the purity of the last KOH washing solutions.

Point analyses show that the major constituents are the 3 oxides SiO_2, CaO and K_2O. The mean percentage of K_2O for all the analysed points is 3,46% and this percentage changes very little from point to point. On the other hand, the contents of SiO_2 and CaO changes considerably between sites from 33.08 to 62.40% for SiO_2 and from 10.27 to 51.38% for CaO irrespective of the C/S value of the original product.

DISCUSSION

The results obtained enable comparison of the morphology and chemical compositions of the natural and synthetic gels. The natural and the synthetic gels placed in the same standard conditions of evolution, present the same morphological characteristics. These two types of gel show a spongy texture, as shown by the S.E.M. at 2400 magnifications. This morphology observed after 28 days seems to be characteristic of very few evolved gels.

Examination of the results in Fig.1 show that the chemical compositions of both types of gel vary in the same fields of concentration. However, we should neglect extreme values of SiO_2 and CaO which probably correspond to distorted analyses due to the presence of grains of sand and cement paste. The disparity between the two groups of points that belong to the synthetic gels and the 100% line is the direct consequence of taking alkalis into account at the time of the analysis. These chemical elements are present inside the solutions trapped by the gels at the time of their dehydration. For the natural gels, this solution is the pore solution of concrete, loaded with sodium and potassium while for the synthetic gels, the washing solutions contain only potassium.

The variation of the values of the CaO and SiO_2 are identical for the two families of gels. Moreover, whatever the original C/S value, the representative points of the synthetic gels are grouped around C/S of 0.48, a value close to the characteristic average (C/S = 0.43) of natural gels (Fig. 2).

All observations suggest a mechanism of formation by instantaneous precipitation of calcium and silica ions from solution.

Examination of the results shows that sodium is not related to Si and Ca. This is further supported in that the washing of synthetic gels with solutions of KOH 0.2M leads to a total elimination of the sodium present from the precipitate. This elimination of sodium is not compensated by the incorporation of potassium which is present, at around 4%, constant from an analysed point to another, irrespective of the C/S ratio. Washing with distilled water of synthetic dried gels under standard conditions at 60°C, quickly leads to a total elimination of the sodium.

All these results confirm the observations of Davies and Oberholster (1988). They show that the Si-Ca structures of gels do not incorporate alkali cations. The sodium and potassium present are simply the result of the trapping of the solution of precipitation into the texture of the gels.

CONCLUSION

This study compared gels developed inside concrete cylinders with synthetic gels, with the following results.

The gels of concrete and the synthetic gels under the same conditions of evolution 60°C, 100% H.R.for 28 days show a characteristic spongy texture. The chemical compositions of the two types of gel, although variable, are grouped around values of C/S = 0.48 for the synthetic gels and C/S = 0.43 for the natural gels. These values appear to be characteristic. The alkalis, sodium and potassium, do not belong to the Si-Ca structure of synthetic gels and this also appears to apply to the natural gels.

The utilisation of characteristic synthetic gels is shown to be a valid method for studying alkali silica gels associated with AAR.

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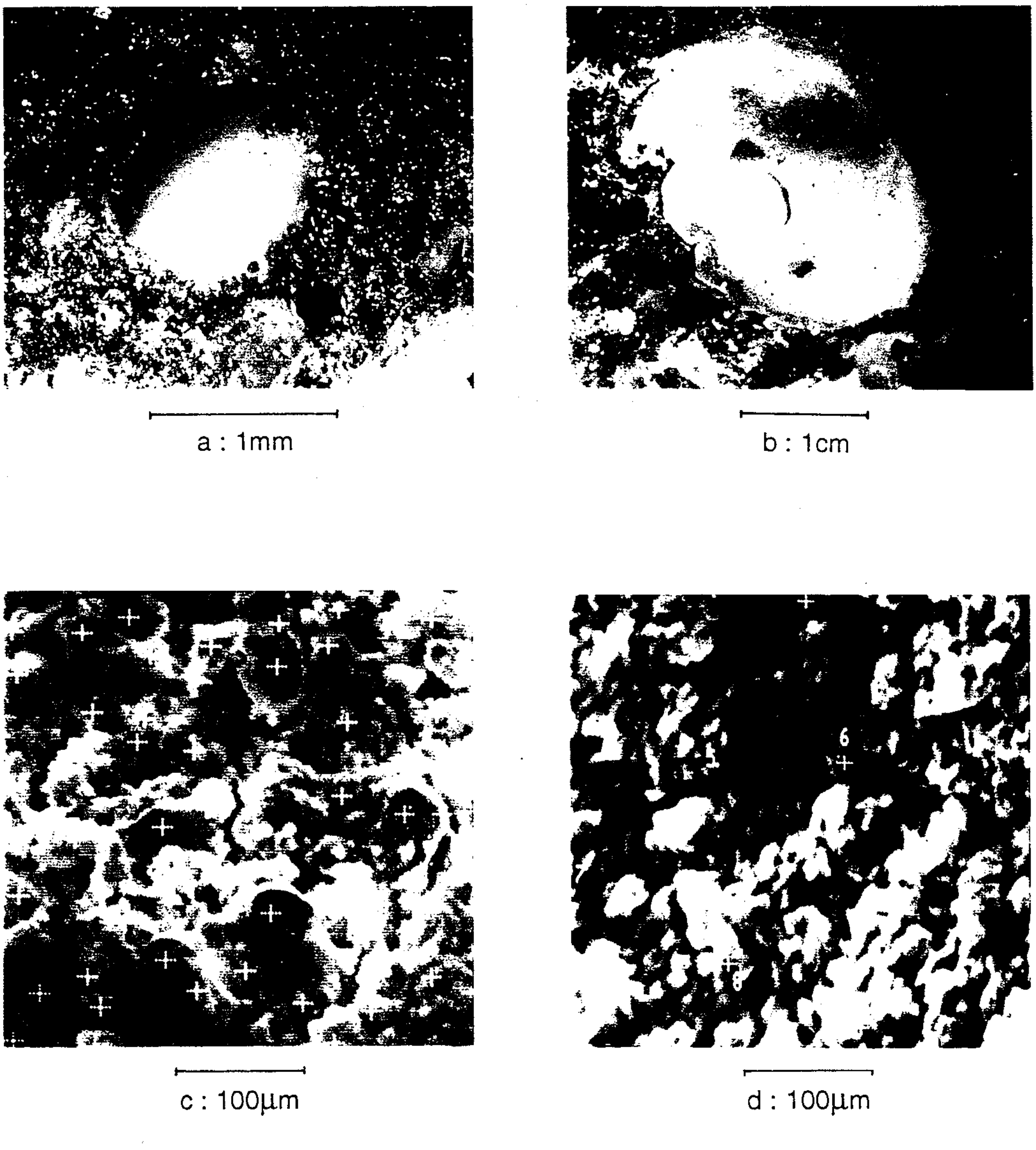

a : 1mm

b : 1cm

c : 100μm

d : 100μm

Fig. 3 a : Fresh gel, still very wet, in a small pore of concrete
b : Fresh gel, partially dehydrated, in a large pore of concrete
c : S.E.M. morphology (secondary electrons) of a natural gel (x2400)
d : S.E.M. morphology (secondary electrons) of a synthetic gel (x2400)