

DO THE ALKALIS BELONG TO THE STRUCTURE OF GEL PRODUCTS OF ALKALI-AGGREGATE REACTION?

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ABSTRACT : From two independent series of experiments, the authors have studied the behaviour of alkalis (Na, Li) in a solution which is in equilibrium with a synthetic gel ($\text{CaO/SiO}_2 = 0.5$) like product of alkali-aggregate reaction.

In the first series of experiments into each p identical gel/solution systems in equilibrium, we first add a similar volume (10 ml) of LiCl solution 0.01 M, following we add $p \cdot 20$ ml of distilled water into the system of order p ($p = 0, 1, 2, \dots$). After a new equilibrium is established, we determine for each gel/solution system the amounts of Na and Li in solution. It appears that the contents of Na and Li versus p comply with the process of dilution.

In a second series of experiments the gel is formed in presence of Li. The remainder of the experimental process and the theoretical approach are unchanged. The results obtained corroborate that Na and Li versus p comply with the process of dilution.

This study demonstrates that Na and Li do not have any interaction with the gel and that they remain in free state in the solution. We can assume that natural gels probably react in the same manner.

keywords : Alkali-aggregate-reaction, chemistry of gels, synthetic gels

INTRODUCTION

The alkali-aggregate reaction (AAR), first identified in the United States by Stanton (1940), appear to be, at the origin of functional disorders, swellings and crackings observed inside ordinary structures.

The products of these AAR are Si-Ca gels, whose limited growth, in the porous medium of concrete induces expansive pressures that can reach 5 MPa (Chongxi. 1986). These are identified as responsible of the swellings and crackings observed. The disorders can strongly reduce the mechanical characteristics of fragile structures like bridges or dams.

Several authors (Brouxel & Valiere. 1992, Buck & Mather. 1969, 1978, Dron, R. & Brivot, F. 1991, Stanton. 1942, Thaulow & Knudsen. 1975) admit that the gels are C-K-S-H, C-Na-S-H, indeed C-K-Na-S-H, with $\text{C}=\text{CaO}$, $\text{S}=\text{SiO}_2$, $\text{K}=\text{K}_2\text{O}$, $\text{Na}=\text{Na}_2\text{O}$ and $\text{H}=\text{H}_2\text{O}$, according to the standard of the cement works. This kind of notation assumes the presence of the corresponding elements inside the structure of these compounds. Moreover, it has been shown (Lombardi *et al.* 1995) that between the oxides which are indicated by the chemical analyses of these gels, only the oxides SiO_2 and CaO are linked, with a strong correlation. As for the present alkalis according to the analyses of these gels, they seem to be easily movable (Davies & Oberholster. 1988 ; Lombardi *et al.* 1995).

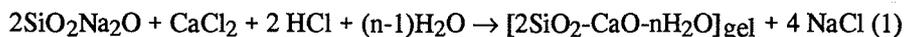
The aim of the following experiments is to specify the behaviour of the alkalis according to the gel/solution system : if they are integrated or not inside the structure of gel or adsorbed at the gel/solution interface.... The experiments use synthetic gels with $\text{C/S}=0.5$, which are as close as possible to the natural gels developed inside the concrete (Lombardi *et al.* 1995).

We have studied the behaviour of sodium and lithium for the following reasons. In this case, the sodium is imperative because it is the major alkali present at the time of the reaction of formation of the synthetic gels. Further, with the potassium, it is the most abundant alkali in concrete. We do not consider potassium because it is

often an impurity inside the metasilicate used for the synthesis of the studied gels and moreover, its capacities of adsorption are very close to those of sodium (for example, on the cationic resins). We choose lithium because it has a high commercial purity without sodium and potassium, and its capacities of adsorption are very low. Thus, it constitutes a good tracer of the aptitude of the gel to integrate alkalis inside its structure. Furthermore, it is one of the easiest elements to determine in solution even at very low concentrations. That is the reason why we have worked simultaneously with two scales of concentration (a few g/l for the sodium, a few mg/l for the lithium), and have thus minimized perturbation of the initial gel/solution system.

EXPERIMENTS

The synthetic gels are prepared according to the method described by Perruchot & Delbove (1982a,b, 1991) : to 20 ml of a solution of $\text{SiO}_2\text{Na}_2\text{O}$ 0.1 M we add 10 ml of a solution of CaCl_2 0.1 M and 2 ml of a solution of HCl 1 M. A gel whose composition is $2\text{SiO}_2\text{-CaO-nH}_2\text{O}$ precipitates quickly, in accordance with the balanced reaction :



The molar efficiency of this reaction, inferred from the amount of residual silica in solution, is 94%.

We study the behaviour of the alkalis in the gel/solution system by dilution of the solution which is in equilibrium with the formed gel. Indeed, because of the dilution of the solution which is in equilibrium with the gel, also by the correlative drop of the pH, we observe a partial dissolution of this gel. Consequently, we simply follow the behaviour in solution of the studied alkalis in order to derive information concerning their integration or not inside the structure of the gel.

We prepared two separate series of experiments. For each series, every experimental result corresponds to an average of measurements based on four very identical and independent experiments.

All the volumetric processes in the making of gels have been done with precision burettes and pipettes (at 1/20 ml), and the chemical analyses have been carried out by spectrometry ICP.

First series :

For the first series of experiments, we initially add to the gel/solution system in equilibrium a constant volume (10 ml) of a solution of LiCl 0.01 M. Then, lithium ion is able to exchange with the gel or to be adsorbed at the interface gel/solution.

The original volume of solution which is in equilibrium with the formed gel is noted V_0 . Its theoretical value is 42 ml, in the absence of notable partial molar effects and/or of an important consumption of water according to the balanced reaction (1). After ultrasonic, shaking, and 48 hours at rest, we centrifuge and determine the concentrations of sodium $[\text{Na}]_0$ and lithium $[\text{Li}]_0$ in the solution which characterizes the original system.

Starting from a gel/solution system prepared exactly in the same way as the previous system, we add a volume $V_a=20$ ml of distilled water and repeat the process of scattering-shaking-rest-parting-chemical analysis. Then, the concentrations of sodium and lithium determined, are respectively $[\text{Na}]_1$ and $[\text{Li}]_1$.

This experiment is reproduced p times, adding $2V_a$ ml of distilled water for the second one, $3V_a$ ml for third, ... pV_a ml for the order p . The concentrations which are established at the end of these experiments are respectively $[\text{Na}]_2, [\text{Na}]_3, \dots, [\text{Na}]_p$ for sodium, and $[\text{Li}]_2, [\text{Li}]_3, \dots, [\text{Li}]_p$ for lithium.

If the sodium in solution is "conservative", in other words, if it does not become a part of the structure of the gel or if it is not adsorbed at the interface gel/solution, it is dependent only on the dilution and verifies :

$$\frac{[Na]_0}{[Na]_p} = 1 + p \frac{V_a}{V_0} \quad \text{with } p = 0, 1, 2, \dots$$

In this case, the graphical representation of $\frac{[Na]_0}{[Na]_p} = f(p)$ is a straight line with a slope $\frac{V_a}{V_0}$.

However, if a sodium fraction is present inside the structure of the gel, or adsorbed, it is released by the partial dissolution of the gel, and :

$$\frac{[Na]_0}{[Na]_p} < 1 + p \frac{V_a}{V_0}$$

It is exactly the same for the lithium.

Second series:

For the second series of experiments, the gel is always formed according to the balanced reaction (1), but once with the presence of LiCl. The LiCl is first introduced into the solution of CaCl₂ at the time of its preparation. Thus, this solution is 0.1 M CaCl₂ and 0.01 M LiCl. In this way, at the time of the process of formation of gel, the lithium is present like the sodium in solution.

Contrary to the first series, the theoretical value of the original volume V₀ of the solution in equilibrium with the gel is just 32 ml. The remainder of the process is not changed and the reasoning concerning these experiments is exactly the same as previously.

RESULTS AND CONCLUSION

The contents and the results are summarized in table 1 for the first series of experiments and in table 2 for the second.

Table 1 Results of the first series of experiments

p	V ₀ +pV _a	[Na] _p (g/l)	[Li] _p (mg/l)	[Na] ₀ /[Na] _p	[Li] ₀ /[Li] _p
0	42	2.270 ±0.015	15.765 ±0.125	1.000	1.000
1	62	1.545 ±0.010	10.545 ±0.045	1.470	1.495
2	82	1.160 ±0.007	7.895 ±0.025	1.960	1.997
3	102	0.940 ±0.005	6.238 ±0.030	2.415	2.530

Table 2 Results of the second series of experiments

p	V_0+pV_a	$[Na]_p$ (g/l)	$[Li]_p$ (mg/l)	$[Na]_0/[Na]_p$	$[Li]_0/[Li]_p$
0	32	3.020 ± 0.015	20.750 ± 0.440	1.000	1.000
1	52	1.895 ± 0.005	12.900 ± 0.025	1.595	1.609
2	72	1.330 ± 0.010	9.460 $\pm 0,025$	2.270	2.195
3	92	1.060 ± 0.030	7.370 ± 0.095	2.850	2.815

According to the precision of the measurements, the corresponding figures, respectively 1a and 1b, 2a and 2b, clearly show that the sodium and the lithium follow the process of dilution. The associated coefficient of correlation and the slope are given on the corresponding figures.

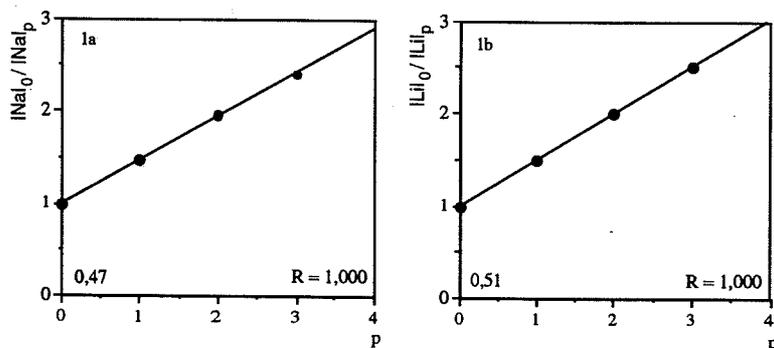


Fig. 1a & 1b The behaviour of sodium (1a) and lithium (1b) in solution for the first series of experiments

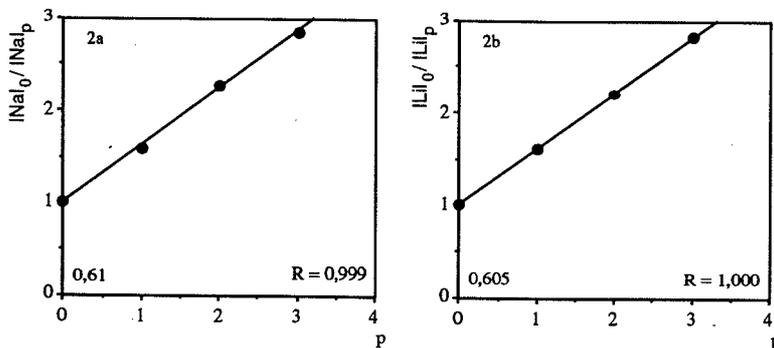


Fig. 2a & 2b The behaviour of sodium (2a) and lithium (2b) in solution for the second series of experiments

Moreover, we know the value of V_a (20 ml), and therefore deduce from the slopes of the straight lines obtained for each series of experiments the corresponding value of V_0 . According to the best experimental uncertainties for the Na analyses, we verify that this value is in accordance with the original theoretical values of each series :

$V_0 = 42.23$ ml for the first and $V_0 = 32.12$ ml for the second series .

All this suggests that the amount of water taking part in the building of the gel is negligible at this scale of analysis.

This study reveals that the alkalis Na and Li in the gel/solution system follow the process of dilution. Consequently, they do not have any interaction with the gel and they remain in free state in the solution.

Inasmuch as the synthetic gels used for this study are close to the natural gels produced by the AAR, we can reasonably assume that the natural gels have the same behaviour relative to alkalis.

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