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EXPERIMENTAL EVALUATION OF COMPOSITION AND VOLUME VARIABILITY OF Ca-Si GELS, FIRST PRODUCTS OF ALKALI SILICA REACTION (ASR)

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ABSTRACT

Synthetic gels prepared from sodium metasilicate and calcium chloride solutions, and placed in similar conditions as those existing within concrete, show a composition range comparable to that of "natural" gels observed in concrete. Whereas synthetic gels are good analogs of natural gels, 8 synthetic gels with a theoretical $(C/S)_0$ ratio : $0.3 \le (C/S)_0 \le 2$, are prepared. Then, the effective composition of each gel is determined from the corresponding residual formation solution at equilibrium. Results show that these gels present an optimum of stability for $(C/S)_g \cong 0.48$ characteristic of gels in equilibrium with their formation solutions.

These experiments also give prominence to the positive variation of the total volume of the reactional system corresponding to a gel formation under constant pressure. The water amount used by the gel formation seems to be negligible. Values obtained for different (C/S)_g ratios comparable to these of natural gels give an estimation of the molar volume of the gels in equilibrium with their respective residual formation solutions. The molar volume of gels produced by ASR can be reasonably evaluated at 21.5 cm³/mole.

Keywords : Alkali Silica Reaction, Ca-Si gels, Composition, Molar volume.

INTRODUCTION

Synthetic Ca-Si gels are good analogs of fresh "natural" gels produced by ASR within concrete (Lombardi et al. 1996 c). From mother-solutions of sodium metasilicate and calcium chloride, the C/S ratios of the synthetic gels are deduced from the chemical composition of the residual formation solutions at equilibrium. The same experimental process conducted with more concentrated solutions and calibrated vessels gives evidence of a positive variation of total volume of the system. Evaluation of the molar volume of gels is deduced as a function of the corresponding C/S ratio.

VARIABILITY OF THE COMPOSITION OF GELS

The purpose of this research is to specify the physical significance of the characteristic range composition of natural gel products of ASR towards their formation process. For that, we studied 8 synthetic gels of various compositions in equilibrium with their formation solutions. Composition of natural gels was often determined by SEM-EDS analysis of solids by several authors such as Brouxel and Valière, 1992; Curtil et al., 1992; Davies and Oberholster, 1988; Habita et al., 1992; Lombardi et al. 1996 c. In this study, the composition of gels is deduced from the compositiont of the formation solutions in equilibrium with their respective residual formation solutions, as a function of their theoretical stoichiometry given by corresponding initial solutions.

The stoichiometric parameter used is the C/S ratio, respectively written $(C/S)_g$ for the gel really formed, and $(C/S)_0$ for the corresponding theoretical value. The range of variation studied, taking into account inherent constraints of the operating conditions, corresponds approximatively to an order of magnitude : $0.3 \le (C/S)_0 \le 2$. In order to obtain a graphical representation allowing a comparative analysis of the variation of C/S within all studied range of stoichiometry, we form the expression :

$$\frac{\Delta(C/S)}{(C/S)_0} = \frac{|(C/S)_0 - (C/S)_g|}{(C/S)_0} = f[(C/S)_0]$$

in which the first member represents, for each experiment, the absolute value of relative difference of C/S between theoretical value and effective value of the gel. Further, this representation is independent of the variation of the sum of concentrations of reacting species.

Method

For any C/S ratio, and taking into account the conservation law of each element, the overall balanced reaction of a gel formation is :

[1] s SiO₂Na₂O + c CaCl₂ + n H₂O + x HCl + y NaOH

$$\rightarrow$$
 [(SiO₂)_s, (CaO)_c, nH₂O] + (2c+x) NaCl + $\frac{x + y}{2}$ H₂O

where s, c, n, x and y are stoichiometric coefficients. Moreover, previous works (Lombardi et al. 1996 a,b) pointed out that the formation of synthetic gels is not consuming water, i.e. $n \approx 0$ in the balanced reaction [1].

All the mother-solution concentrations are 0.1 M in each species. Thus, the volumes of used solutions represent the proportions of reacting species according to s, c, x and y in the balanced reaction [1]. The general equation between x, y, c and s is equivalent to the conservation law of Na and Cl:

$$2c + x = 2s + y$$

then, by introducing the C/S parameter and after rearrangement :

$$2s(C/S - 1) = y - x$$

In these experiments, the synthetised gels correspond always conventionally to s = 1 for 20 ml of 0.1 M SiO₂Na₂O solution and the precedent equation can be written :

$$2(C/S - 1) = y - x$$

According to the C/S value, three cases can be considered :

C/S > 1 ⇔ y > x; for x = 0, it comes y_{min} such as

$$y_{min} = 2(C/S - 1)$$

- $C/S = 1 \Leftrightarrow y = x; x_{min} = y_{min} = 0$
- C/S < 1 ⇔ y < x; for y = 0, it comes x_{min} such as

$$x_{min} = 2(1 - C/S)$$

So, for each theoretical $(C/S)_0$ value, the required volume of 0,1 M HCl or NaOH solution in overall balanced reaction [1] is respectively 20 x_{min} ml or 20 y_{min} ml.

Experiments are performed without stirring at 20 °C, 1 bar. Each experiment is independent of the others, and run in duplicates. By reason of addition of x ml HCl or y ml NaOH solution according to the C/S selected value, the pH at equilibrium was varied between 11.6 and 13.6. For the same reason, Na was not determined, the more that the Ca-Si structures of gels do not seem incorporate alkali cations (Lombardi et al. 1996 a, b). After 21 days, each equilibrium is fully reached (Perruchot 1973, Perruchot et al. 1991) and chemical analyses are performed by ICP on each solution in equilibrium with the corresponding gel. The molar efficiency of the reaction is deduced from amount of silica measured in the residual formation solution in equilibrium with the gel : it is better than 90 % even for low (C/S)₀ values.

Results

The data and the results of experiments are given in Table 1.

(C/S)0	Si sol	Ca sol	Si gel	Ca gel	$(C/S)_g$	$\Delta(C/S)$
	mg/l	mg/l	10-3 moles	10-3 moles		(C/S)0
2	0.38	473.60	1.999	2.816	1.409	0.296
2	0.39	487.80	1.999	2.781	1.391	0.304
1.2	2.14	190.10	1.996	2.153	1.079	0.101
1.2	1.91	208.70	1.996	2.129	1.066	0.111
1	3.99	104.10	1.994	1.896	0.951	0.049
1	4.88	115.90	1.993	1.884	0.945	0.055
0.8	35.86	119.40	1.944	1.469	0.756	0.055
0.8	54.41	133.30	1.914	1.453	0.759	0.051
0.6	101.60	121.00	1.826	1.055	0.578	0.037
0.6	83.00	113.20	1.858	1.064	0.573	0.045
0.5	105.90	106.30	1.811	0.867	0.479	0.042
0.5	112.30	109.70	1.799	0.863	0.480	0.041
0.5	110.60	106.40	1.803	0.867	0.481	0.038
0.5	112.40	110.10	1.799	0.862	0.479	0.041
0.4	118.30	106.40	1.780	0.662	0.372	0.071
0.4	122.10	102.00	1.773	0.667	0.376	0.059
0.3	137.30	103.60	1.735	0.460	0.265	0.116
0.3	137.40	103.70	1.735	0.460	0.265	0.116

 TABLE 1 : Variation of C/S of Gels in Equilibrium with Respective Residual Formation

 Solutions : (C/S)0 : theoretical value ; (C/S)g : effective value.

The curve $\frac{\Delta(C/S)}{(C/S)_0} = f[(C/S)_0]$ drawn from these results (Fig. 1) shows a distinct minimum centered on $(C/S)_0 = 0.5$ for $(C/S)_g \approx 0.48$.



Fig. 1 : Relative variation of the effective value $(C/S)_g$ as a function of the theoretical value $(C/S)_0$ for 8 synthetic gels. Ordinate : $\frac{\Delta(C/S)}{(C/S)_0}$; abscissa : $(C/S)_0$.

The value $(C/S)_g \approx 0.48$ corroborates the one settled by SEM-EDS analysis of a synthetic gel of $(C/S)_0 = 0.5$ (Lombardi et al. 1996 c, d). This value $(C/S)_g \approx 0.48$ is then interpreted as optimum of stability of gels in equilibium with the residual formation solutions. In the same way, and as far as the formation mechanism is common for both natural and synthetic gels, by coprecipitation of Ca and silicate ions in solution, the value C/S = 0.43 (Lombardi et al. 1996 c, d) is interpreted as optimum of stability of natural gels in equilibrium with their formation solutions, in presence of reactive mineral phases, portlandite and silica.

VARIABILITY OF THE VOLUME OF GELS

The previous experiments were also conducted using mother-solution concentrations 0.5 M in each species. In these conditions, the amount of silica is almost totally consumed by the formation of gels, and the quantities of gels are more important. In these conditions, variations of volume are more easily measurable. For that, we used always the same calibrated vessels (jars, pipettes) for all experiments.

Method

The different values of (C/S)₀ are obtained by dilution of 0.5 M mother-solutions. The sum of initial volumes of reactants in the balanced reaction [1] is always exactly 250 ml. For each experiment, the positive measured variation of overall volume, after formation of gel, is ΔV_m . As a first approximation, the partial molar volumes of reacting species in solution are not taken into account. Likewise, the correction for the volume of water formed given by the balanced reaction [1] for each (C/S)₀ value is approximated to 18 cm³ per mole as for pure water. This volume of formed water is substracted from ΔV_m . Thus, the residual volume ΔV_g is attributable to the number of moles of gel formed within the accuracy of experiments. According to the definition of the compositional effective parameter (C/S)_g and the quantity s of silica consumed, the molar volume of gel V_g, is given by :

$$V_g = \frac{1}{s} \cdot \frac{\Delta V_g}{\left[1 + (C/S)_g\right]}$$

Experiments are performed without stirring at 20 °C, 1 bar as previously. Each experiment is independent of the others, and repeated at least three times. Taking into account of the low accuracy of the measures, the results reported in Table 2 are means of the values which display a dispersion lower than 10 %.

Results

The data and the results of experiments are given in Table 2.

TABLE 2 : Variation of the Overall Volume ΔV_m of the System as a Function de $(C/S)_g$ and Evaluation of the Molar Volume V_g of Gel in Equilibrium with the Corresponding Residual Formation Solution. $(C/S)_0$: theoretical value ; $(C/S)_g$: effective value.

(C/S) ₀	(C/S)g	SiO ₂ gel	H ₂ O	ΔV_m	ΔVg	Vg 3/mala
		10 ⁻⁵ moles	10 ⁻⁵ moles	(cm ³)	(cm ³)	cm ² /mole
2	1.451	25	25	1.750	1.300	21.22
1.2	1.072	25	5	1.227	1.137	21.95
1	0.948	50	0	2.000	2.000	20.51
0.8	0.757	50	10	1.900	1.720	19.57
0.6	0.575	25	10	1.000	0.820	20.82
0.5	0.480	50	25	2.200	1.750	23.65
0.4	0.375	25	15	1.045	0.775	22.56
0.3	0.265	25	17.5	0.864	0.549	17.35

The curve $V_g = f[(C/S)_g]$ drawn from these results (Fig. 2) is noticeably constant for $(C/S)_g \ge 0.4$. Then the molar volume of gels Vg appears close to 21.5 cm³/mole for $0.4 \le (C/S)_g \le 1.5$ within the limits of this experimental approach.



Fig. 2 : Variation of the molar volume of gels as a function of the effective value (C/S)g for 8 synthetic gels.

CONCLUSIONS

According to the hypothesis of a common mechanism of formation of both natural and synthetic gels by instantaneous coprecipitation from solutions of Ca and silicate ions (Lombardi et al. 1996 c,d), this study shows that :

- the fresh ASR gels in equilibrium solely with their formation solutions present an optimum of stability for $(C/S)_g \approx 0.48$;

- the apparent molar volume V_g of these fresh gels can be reasonably evaluated close to 21.5 cm³/mole within the limits of our experiments.

The positive variation of the total volume of the system corresponding to a fresh gel formation under constant pressure corroborates the expansive character of ASR within concrete in presence of alkaline solutions.

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