



Study of the Influence of Alkaline Ions (Li, Na and K) on the Structure of the Silicate Entities in Silico Alkaline Sol and on the Formation of the Silico-Calco-Alkaline Gel

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Abstract. The study of silico-calco-alkaline gel is essential to warn against the degradation of concrete due to the alkali-silica reaction. In the laboratory, those gels are simulated by the destabilization of a silico-alkaline sol by calcium ions. Their speed of formation depends on the alkali species. The influence of alkaline ions (Li, Na and K) on the structure of silicate entities in sol and on the gel formation has been studied. The state of polymerization of the silico-alkaline sol was determined by NMR and depends on the alkali species and the molar ratio ($Rm = [\text{SiO}_2]/[\text{A}_2\text{O}]$ with $\text{A} = \text{Li, Na or K}$). It appears that lithium enhances the polymerization. By scattering techniques (SAXS and ELS), the evolution of size and number of scattering particles during gelation can be determined from scattering curves with Guinier approximation. The mechanism of gelation appears like a hierarchic structure composed with several discrete sizes.

Keywords: silicate, alkaline, gelation, kinetics

Introduction

Concrete is a porous material comprised of aggregates immobilized in a cement paste. If the aggregates contain reactive silica, the interaction between these aggregates and the various ions present in the concrete pore solution (hydroxide, alkaline, calcium,...) induces the formation of calcium alkaline silica gel which can subsequently lead to cracking of the concrete. This reaction is commonly called the alkali-silica-reaction (ASR).

In our laboratory, this system is simulated by destabilization of alkaline silicate sols by a calcium salt ($\text{Ca}(\text{OH})_2$ portlandite). The preparation of these gels consists of two stages:

- (1) Dissolution of the silica by hydroxide ions leading to the formation of a concentrated silico-alkaline

solution. The maximum silica concentration is defined as the pessimum condition ($[\text{SiO}_2]_{\text{max}} = 1.5 \text{ mol} \cdot \text{l}^{-1}$) [1].

- (2) Destabilization of the alkaline silicate solution by calcium ions leading to the formation of a silico-calco-alkaline compound (gel or precipitate).

Other works [2, 3] have shown that, when the molar ratio ($Rm = \text{SiO}_2/\text{A}_2\text{O}$; $\text{A} = \text{Na or K}$) is low, the silico-alkaline solution contains weakly polymerized silicate entities. Increasing the molar ratio strongly enhances the degree of polymerization of these solutions. When the ratio is higher than 2, Iler [4] and Harris [2] have shown that the solution can be considered to be colloidal one (entities of between size 10 and 1000 Å). When such sols ($Rm > 2$) are destabilized by calcium ions, the compound formed is a gel, while if $Rm < 2$,

it is a precipitate. Calcium ions act as a “catalyst” by bringing together two silicate entities and then being replaced by a siloxane bond.

There is a great disparity in gelation times depending on the alkali species and the molar ratio. Gels formed with sodium have the shortest gelation time, at constant calcium concentration, independent of the molar ratio (2 or 3).

The aim of this study is to explain these differences by determining, first, properties of sols by ^{29}Si Nuclear Magnetic Resonance (NMR) and then to determine the structure of gel by Small Angle X-ray Scattering (SAXS) and Elastic Light Scattering (ELS).

Experimental

Sols are obtained by mixing silica (silicagel, Merck chromatography), an alkali (Li, Na or K) oxide and water for several days, until thermodynamic equilibrium is reached (no filtration). For both molar ratios of 2 and 3, the silica concentration is maintained constant at $1.5 \text{ mol} \cdot \text{l}^{-1}$.

^{29}Si NMR spectra of the sols were recorded on a Bruker DRX500 spectrometer operating at 99.36 MHz (the silicon-29 frequency resonance). PTFE sample tubes were used (4 mm o.d.), held vertically a 5 mm o.d. glass tube. Heavy water (10%) was added to the samples to lock the spectrometer. A pulse width of 90° ($10.8 \mu\text{s}$) was used with a repetition time of 90 s. FIDs were acquired over a sweep width of 20 kHz (200 ppm) using 32 K data. A “blank” FID was acquired, corresponding to the background of the probe, and was subtracted from each data set. A line broadening of 8 Hz was applied, giving a satisfactory signal-to-noise ratio.

The samples were sonicated after calcium hydroxide was added to the sols. The samples were then centrifuged so as to obtain homogeneous destabilized sols. The gelation time was determined by observing when the meniscus in a container no longer remained

horizontal when the container was tilted. These gelation time results were very reproducible ($\sim 5\%$).

Kinetics of gelation have been followed *in situ* by two scattering techniques. SAXS curves have been obtained by LURE (Orsay) and those of ELS in our laboratory (LRRS-Dijon). They measure the angular dependence of the intensity scattered by a sample with heterogeneities in electron density (SAXS) and in refraction index (ELS). The domain studied is not the same because the wavelength used is different. The SAXS technique scattering vector domain observed was: $5 \times 10^{-3} \text{ \AA}^{-1} < q_{\text{SAXS}} < 7 \times 10^{-2} \text{ \AA}^{-1}$ and the ELS one was $4 \times 10^{-4} \text{ \AA}^{-1} < q_{\text{ELS}} < 2 \times 10^{-3} \text{ \AA}^{-1}$. There is a blind zone ($5 \times 10^{-3} \text{ \AA}^{-1} < q < 2 \times 10^{-3} \text{ \AA}^{-1}$) which could be reached by SANS. The SAXS curves of the samples were treated by subtracting the background and the corresponding nondestabilized sol curve.

Results and Discussion

Analysis of Sols

^{29}Si NMR was performed on silico-alkaline sols. It gives information about the degree of connectivity of silicon atoms. The usual notation is Q^n where Q represents a silica tetrahedron and n is the number of tetrahedra connected to this one. Structural distributions for those solutions are presented in Table 1.

A mean degree of connectivity was calculated using:

$$\bar{n} = \frac{\sum_n n \times Q^n}{\sum_n Q^n}$$

to account for the state of polymerization of the silico-alkaline solutions. The evolution of n as a function of the alkali ion present and the molar ratio is shown in Fig. 1.

For all the alkali ions, the mean degree of connectivity increases with the molar ratio. This is in agreement with the results for sodium reported by Harris [4].

Table 1. Structural distributions for aqueous silico-alkaline sols with different molar ratios (2 and 3); constant silica concentration ($[\text{SiO}_2] = 1.5 \text{ mol} \cdot \text{l}^{-1}$).

Structural unit (%)	$\text{SiO}_2/\text{Li}_2\text{O} = 2$	$\text{SiO}_2/\text{Li}_2\text{O} = 3$	$\text{SiO}_2/\text{Na}_2\text{O} = 2$	$\text{SiO}_2/\text{Na}_2\text{O} = 3$	$\text{SiO}_2/\text{K}_2\text{O} = 2$	$\text{SiO}_2/\text{K}_2\text{O} = 3$
Q^0	9.72	2.85	9.62	7.39	10.3	10.03
Q^1	12.47	7.15	17.73	14.55	13.8	11.28
Q^2	18.53	12.01	28.43	11.43	35.7	13.5
Q^3	59.28	53.83	44.22	66.63	40.2	65.19
Q^4	0	24.16	0	0	0	0

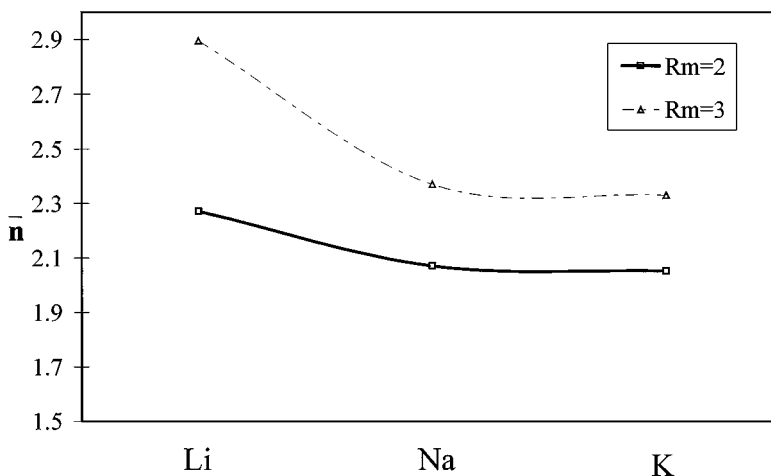


Figure 1. Evolution of mean degree of connectivity of silico-alkaline solutions ($[\text{SiO}_2] = 1.5 \text{ mol} \cdot \text{l}^{-1}$) as a function of alkali ion and molar ratio ($Rm = [\text{SiO}_2]/[\text{A}_2\text{O}]$ with $A = \text{Li, Na and K}$).

Moreover, it appears that with lithium, the degree and polymerization is higher than in the case of sodium or potassium, independent of the molar ratio.

Gelation Time

The influence of the alkali species and the molar ratio on the gelation time is shown in Fig. 2.

At a constant calcium concentration and independent of the molar ratio, gelation time with sodium is shorter than the gelation time with lithium and potassium.

When the molar ratio increases, the gelation time increases, except if potassium is present. For a molar ratio of 2, the gelation time with potassium is the greatest; whereas for a molar ratio of 3, the gelation time with lithium is the greatest.

Structure of Gels

Figure 3 represents scattering curves by SAXS and ELS at different times (times normalized by gelation time) for one gelation condition.

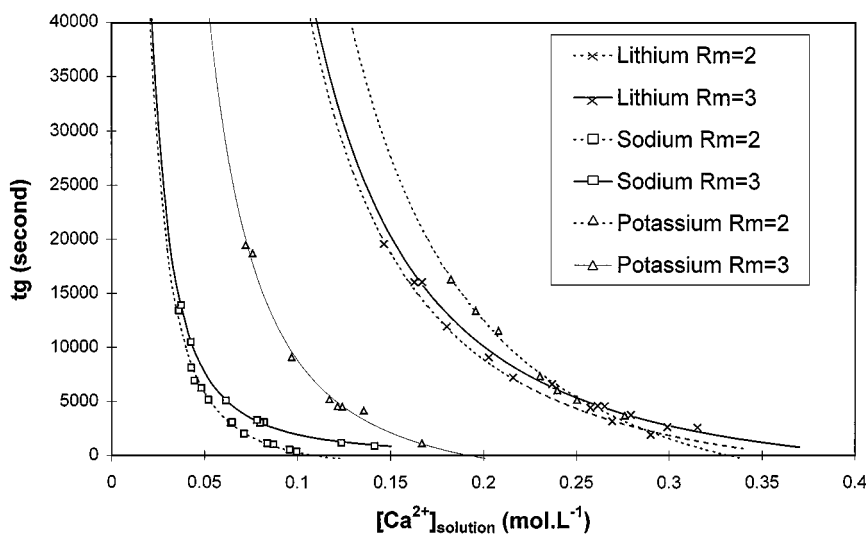


Figure 2. Evolution of gelation time as a function of calcium concentration in solution (after centrifugation).

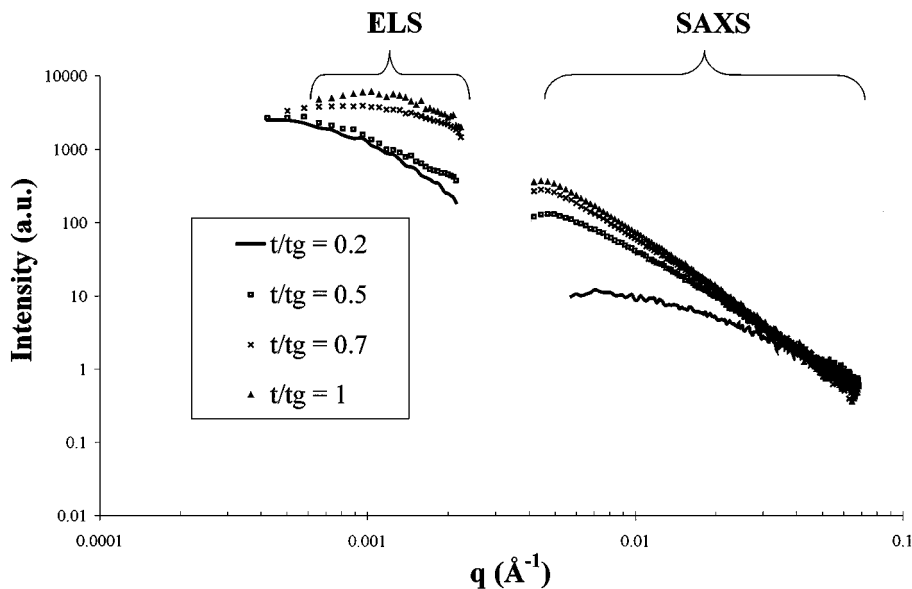


Figure 3. SAXS (Small Angle X-ray Scattering, LURE Orsay) and ELS (Elastic Light Scattering) curves for a silico-calco-sodium gel ($Rm = 2$; $[\text{Ca}(\text{OH})_2] = 0.08 \text{ mol} \cdot \text{l}^{-1}$). Measurements made in situ; time normalized by gelation time.

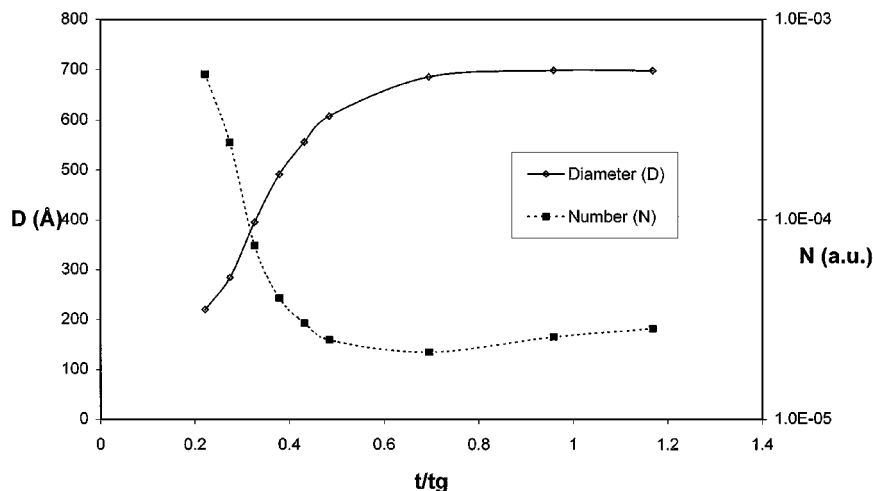


Figure 4. Evolution of size and number of particles by SAXS as a function of time (normalized by gelation time) for a silico-calco-sodium gel ($Rm = 2$; $[\text{Ca}(\text{OH})_2] = 0.08 \text{ mol} \cdot \text{l}^{-1}$).

In each case, the intensity scattered has a plateau at low angles which can be approximated by Guinier's law [5]:

$$I_{\text{scattered}} = I_0 \times \exp\left(-\frac{q^2 \times Rg^2}{3}\right)$$

$$\text{with } D = 2 \times \sqrt{\frac{5}{3}} \times Rg.$$

Using these relationships, information on the size ($D = \text{diameter}$) of particles is obtained from scattering curves for qRg smaller than 1. The evolution of particle number N (qualitative) is deduced from I_0 (the extrapolated intensity to $q = 0$) by the relation:

$$I_0 \propto NR^6.$$

After the Guinier zone (in SAXS and ELS), the scattered intensity does not follow a power law as seen with

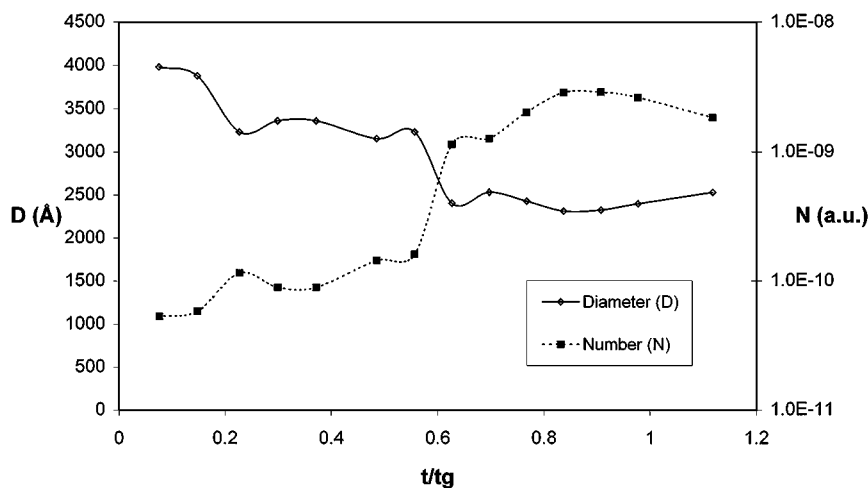


Figure 5. Evolution of size and number of particles by ELS as a function of time (normalized by gelation time) for a silico-calco-sodium gel ($Rm = 2$; $[Ca(OH)_2] = 0.08 \text{ mol} \cdot \text{l}^{-1}$).

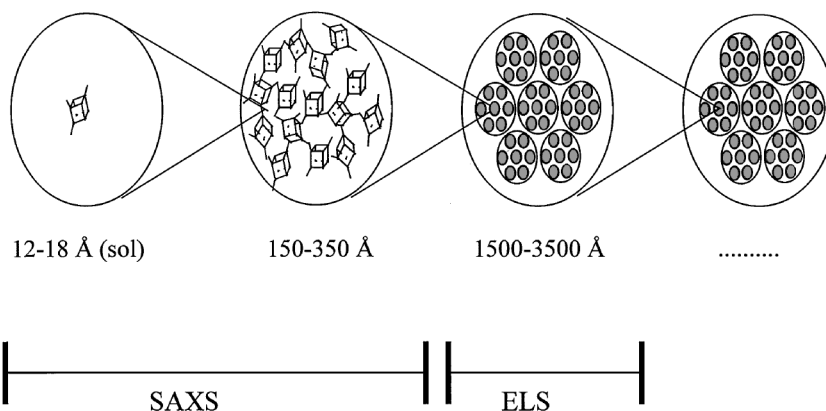


Figure 6. Hierarchic structure for the mechanism of gelation.

fractal systems. Porod's law ($I \sim q^{-4}$)⁷, for large angles, is also not observed in this study.

Figures 4 (SAXS) and 5 (ELS) show the evolution of particle size and particle number during silico-calco-sodium gel formation.

It can be seen that particles reach an equilibrium size in the "two windows of observation." The number of smaller particles decreases (shown by SAXS), while the number of larger particles increases (shown by ELS). Smaller particles appear to be absorbed by larger particles. The reaction kinetics are similar and they are independent of the alkali present, meaning that the mechanism of gelation is the same.

These results show that three or more discrete sizes of particles are present: particles with the same size of

initially sols, particles detected by SAXS and particles detected by ELS.

A hierarchic structure (Fig. 6) can be proposed as the structure of silico-calco-alkaline gel.

Conclusion

This study shows the influence of alkali ions on silico-alkaline sols; most notably lithium ions increase the degree of polymerization of silicate entities.

When calcium ions are added, we observe some variation of the gelation time dependent on the alkali ion and the molar ratio. However, the variations in gelation time do not follow the variations in the degree

of connectivity. Therefore, the gelation time is independent of the structure of the silicate entities in sol.

If the interaction between silicate entities and alkali ions is strong, calcium ions cannot readily replace the alkali ions [6]. The observed differences in gelation time are probably due to this interaction.

The mechanism of gelation induces a hierarchic structure of discrete sizes. More experiments must be done to examine the unobserved domain between SAXS and ELS experiments.

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