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Polymerization of alkaline-calcium-silicate hydrates obtained by interaction between alkali–silica solutions and calcium compounds. A ^{29}Si nuclear magnetic resonance study

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Alkali–silica solutions containing varying amounts of silica and alkali ions have been prepared. Solids were obtained by interaction of these solutions with calcium hydroxide, calcium chloride or calcium sulphate. A ^{29}Si nuclear magnetic resonance study has been carried out on these products during the initial and final stages of the synthesis. Three major kinds of solids appear in the $CaO–Na_2O(K_2O)–SiO_2$ phase diagram; a chain-like nanocrystalline solid, a plate-like amorphous solid, and a three-dimensional amorphous network solid. A relationship between the initial system (i.e., the initial solution) and the final system (i.e., the solid plus the residual solution) is established. The solid is found to have a higher degree of polymerization than the initial solution while the residual solution is mearly an alkali–silica solution without calcium ions.

1. Introduction

In a wet concrete, the cement or the aggregates may release alkaline ions which results in a high pH solution being present in the cement micropores. In the presence of this alkaline solution, the silica provided by the aggregates may pass into solution. An interaction with the calcium hydroxide present in the medium leads to reactions which can provoke the occurence of microfissures, and with time the destruction of the structure. This reaction is known as the alkali–silica reaction (ASR).

Different methods to synthesize products which may be considered relevant to the study [1–4] of the alkali–silica reaction have been proposed.

In a previous paper [5], ASR was studied by mixing an alkali–silica solution and calcium chloride. It was shown by using ^{29}Si nuclear magnetic resonance (NMR) spectroscopy that the connectivity of the silicate ions in the solution governs the degree of polymerization of the solid. A relationship was also observed to exist between the CaO/SiO_2, K_2O/SiO_2 (or Na_2O/SiO_2) ratios and the structure of the solids. For higher ratios, the solid was a nano-crystalline alkaline–calcium–silicate hydrate and for lower ratios, the solid was analogous to a siliceous gel. The nature of the alkali ion, i.e., potassium or sodium, has no significant influence on the structure of the solid.

In the first part of the present work, a calcium compound, namely either calcium chloride, calcium sulphate or calcium hydroxide, was mixed with an alkali–silica solution to produce a solid alkaline–calcium–silicate hydrate in equilibrium with a residual alkali solution. Concerning notation, synthesized products involving $CaSO_4$ or $CaCl_2$ are referred to as type I products, and the other products are referred to as type II products.

In this paper, a ^{29}Si NMR study was carried out on the type I products (initial solutions and obtained solids). Attention has been focused on the influence of the counter-ion of the calcium compound and on lower CaO/SiO_2 ratios. This study allowed the determination of three kinds of solids in the $CaO–Na_2O(K_2O)–SiO_2$ phase diagram. The relationship between the structure of the solids and the structure of the initial solutions is established and it is clear that the solids are more polymerized than the initial solutions. This trend is confirmed by the study of the silicate species balance in the initial and final systems. These facts lead to a description of the polymerization of alkaline–calcium–silicate solids obtained by interaction between alkali–silica solutions and calcium compounds.

2. Experimental procedures

2.1. Synthesis

By the action of calcium ions on alkali–silica solutions, two series of solids have been studied: type I and type II products. In the first instance, two calcium compounds were used in the synthesis: calcium sulphate and calcium chloride. These two compounds were used in order to understand the influence of the dissolution kinetics of the calcium compound and the effect of the counterion on the solid structure. For a more realistic approach, calcium hydroxide was used. Calcium hydroxide is present in cement as portlandite and can interact with the solution.

2.1.1. Type I products

Prior to the addition of calcium ions, the alkali concentration in the initial solution was fixed at 0.7 mol l^{-1}. This concentration is approximately that of the alkali concentration found in the pore fluid inside concrete. To obtain solutions with a SiO_2/Na_2O ratio less than 1, a solution of sodium metasilicate ($SiO_2/Na_2O \cong 1$) was used. For higher ratios, a solution of sodium silicate ($SiO_2/Na_2O \cong 3$) was used. Calcium ions were introduced in the form of either calcium sulphate or calcium chloride.

The $CaSO_4.2H_2O$ was introduced into the reaction in the form of a powder to form concentrations of 0.03 mol l^{-1}. A volume of 0.4286 l of a calcium chloride solution of concentration 0.03 mol l^{-1} was added to 1 l of an alkali–silica solution. The obtained solids were filtered, and then washed with acetone and ether.

Chemical analysis was conducted using the flame absorption spectroscopy technique on a Perkin-Elmer 3030 spectrometer following the procedure of reference [6] namely the Tenoutasse method. The solids were dissolved in hydrochloric acid, hydrofluoric acid and in boric acid and the obtained solutions were studied by flame spectrometry. An analysis of the residual solution was also performed which showed the absence of calcium ions in the residual solution.

All the products, initial solutions and solids, were studied by ^{29}Si NMR.

2.1.2. Type II products

Type II solids were obtained by the reaction of calcium hydroxide with alkali–silica solutions with the silica concentration varying between 0.25–1.5 mol l^{-1} in steps of 0.25 mol l^{-1}. The potassium hydroxide concentration in these solutions varied between 0.25–2 mol l^{-1} in steps of 0.25 mol l^{-1}. To achieve these concentrations, a 3.7 mol l^{-1} SiO_2 and a 0.97 mol l^{-1} KOH potassium silicate solution were used.

To obtain the solids, calcium hydroxide was added by soaking 1.0 g of calcium oxide in 20 ml of hot water; then 80 ml of alkali–silica solution were added with an increased molarity of 25% to take into account the dilution induced by the water in the calcium hydroxide solution.

The thus obtained solids were washed with an equivalent amount of water and then centrifuged. This operation was repeated a total of two times.

Chemical analysis was performed using the inductive coupling plasma (ICP) technique for which the solid product was crushed and sieved to a size less than 80 μm and then fused with lithium tetraborate. The pearl thus obtained was then reacted with a 0.02 mol l^{-1} nitric acid solution. These solutions were then analysed by ICP spectroscopy.

2.2. NMR spectroscopy

2.2.1. ^{29}Si NMR spectroscopy of the solutions

The spectra of the type I solutions were measured on a Bruker WM 250 spectrometer in a 5.87 T field and at a frequency of 49.69 MHz using the single pulse mode. The sweep width was 3000 Hz, the recycle delay was 1.4 s, the pulse width was of 21 μs corresponding to a flip angle of 30° and the number of scans varied from 3000 to 40 000, depending on the silica concentration in the solution.

The spectra of the type II solutions were measured on a Bruker AM 500 spectrometer using the single pulse mode, in a 11.74 T field and at a frequency of 99.4 MHz. The sweep width was 5000 Hz, the recycle delay was 1.4 s and the pulse width was 21 μs corresponding to a flip angle of Π/2. In the "precipitate" system (see below) the number of scans was 30 000 for each solution. In the "gel" system (see below) the number of scans was 45 000 for the initial solution and 200 000 for the residual solution, depending on the silica concentration in the solution.

2.2.2. NMR spectroscopy of the solids

Solid state spectra were measured on a Bruker CXP 300 spectrometer, in a 5.87 T field and at a frequency of 59.62 MHz using magic angle spinning. The sweep width was 20 kHz, the recycle delay was 300 s, the pulse width was 5 μs corresponding to a flip angle of Π/2 and the number of scans was 100. Spectra were analysed using the Q^n classification, where Q stands for the SiO_4^{4-} tetrahedron and the superscript n refers to the number of tetrahedra linked to the preceding tetrahedron [7]. Thus, n varies between 0 and 4.

The solid state spectra were decomposed and integrated with an in house written program in order to obtain the Q^n populations.

3. Results and discussion

First of all, care has to be taken with the treatments received by the solid products. As has been shown in previous work [5], washing the solid too vigorously with water can affect the structure. However not washing the solid at all is also undesirable for the study of the solid. In Fig. 1 the effects of not washing and of

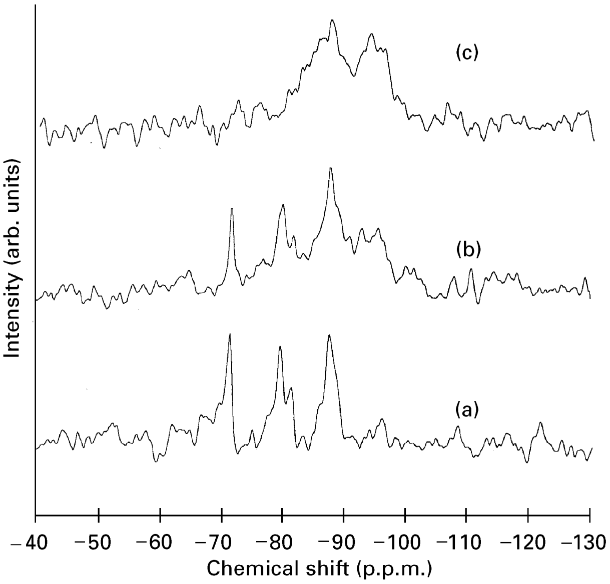

Figure 1 Effect of the washing; ^{29}Si NMR spectra of a (a) residual solution, (b) unwashed gel, (c) washed gel.

a "soft" washing can be seen. A comparison between the residual solution (spectrum a, Fig. 1), the unwashed solid (spectrum b, Fig. 1) and the washed solid (spectrum c, Fig. 1) shows that the peaks seen on the unwashed solid spectrum are due to residual solution that remains adsorbed onto the solid. The remaining peaks on the washed solid are solely related to the solid phase.

3.1. The CaO–Na_2O(K_2O)–SiO_2 phase diagram

The results of the chemical analysis of the solid products are shown in the ternary diagram, Fig. 2, and listed in Tables I–III.

In the lower part of the diagram are the precipitates. Interaction of the solution with calcium compounds leads to a precipitate which sinks in the beaker. The precipitate is a nano-crystalline compound with an X-ray pattern (see for example [4]) analogous to a cementitious calcium-silicate-hydrate. The upper region in the diagram corresponds to macroscopically homogeneous gels impregnated by a serum of potassium silicate solution. The gel fills the volume originally occupied by the initial solution and the X-ray pattern [4] of the gel is typical of an amorphous material.

Three typical NMR spectra of the solutions and the solids obtained by adding a calcium compound are shown in Fig. 3. The first spectrum of the solids (spectrum (d)) is the spectrum of a chain-like cementitious calcium-silicate hydrate constituted of Q^1 and Q^2 entities. The NMR spectra of the solids taken in the precipitate domain present the same general features as above: namely Q^1 and Q^2 entities in differing amounts that depend on the concentrations of the individual ions present in the solid.

The two other solid state spectra (spectra (e) and (f)) belong to the gel domain and are somewhat different from each other. Spectrum (e) exhibits Q^2 and Q^3

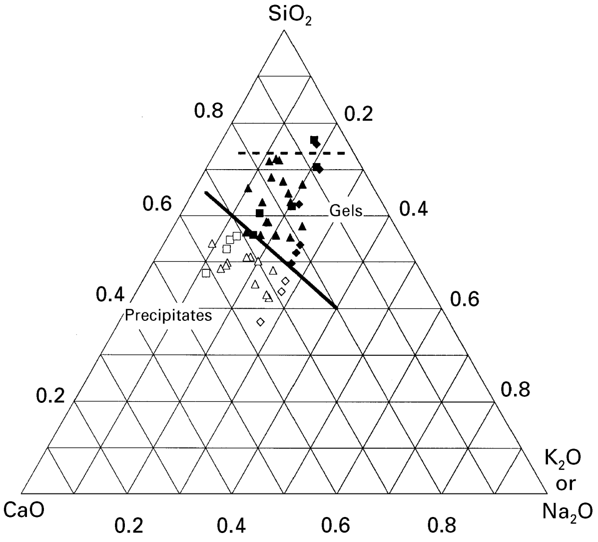

Figure 2 Ternary phase diagram of the solids. Key: (□) type I, $CaSO_4$ precipitate; (■) type II, $CaSO_4$ gel; (◇) type I, $CaCl_2$ precipitate; (◆) type I, $CaCl_2$ gel; (△) type II, $Ca(OH)_2$ precipitate and (▲) type II, $Ca(OH)_2$ gel.

TABLE I Chemical analysis of the type I products produced by the addition of $CaSO_4$

Initial solutions		Solids obtained by $CaSO_4$ action		
NaOH ($mol\,l^{-1}$)	SiO_2 ($mol\,l^{-1}$)	SiO_2 ($mmol\,g^{-1}$)	CaO ($mmol\,g^{-1}$)	Na_2O ($mmol\,g^{-1}$)
0.7	0.035	5.97	5.18	1.43
0.7	0.105	6.79	4.46	1.63
0.7	0.140	7.42	4.48	1.66
0.7	0.210	6.92	3.90	1.64
0.7	0.263	6.82	3.43	1.98
0.7	0.350	7.65	3.09	1.90
0.7	0.525	7.82	2.22	2.57
0.7	0.788	8.96	1.10	2.65
0.7	1.050	9.91	0.80	2.27

TABLE II Chemical analysis of the type I products produced by the addition of $CaCl_2$

Initial solutions		Solids obtained by $CaCl_2$ action		
NaOH ($mol\,l^{-1}$)	SiO_2 ($mol\,l^{-1}$)	SiO_2 ($mmol\,g^{-1}$)	CaO ($mmol\,g^{-1}$)	Na_2O ($mmol\,g^{-1}$)
0.7	0.035	4.26	4.14	3.09
0.7	0.105	4.71	3.11	3.00
0.7	0.140	5.04	2.95	3.00
0.7	0.210	6.01	2.89	3.22
0.7	0.263	5.49	2.30	2.78
0.7	0.350	5.27	1.98	2.57
0.7	0.525	6.77	1.73	2.33
0.7	0.788	7.76	0.92	2.40
0.7	1.050	9.03	0.74	2.20

TABLE III Chemical analysis of the type II products produced by the addition of $Ca(OH)_2$

Initial solutions		Solids obtained by $Ca(OH)_2$ action		
KOH ($mol\,l^{-1}$)	SiO_2 ($mol\,l^{-1}$)	SiO_2 ($mmol\,g^{-1}$)	CaO ($mmol\,g^{-1}$)	K_2O ($mmol\,g^{-1}$)
0.25	0.25	8.76	5.97	1.49
0.25	0.5	10.57	3.82	1.62
0.5	0.25	7.86	5.67	2.24
0.5	0.5	9.01	3.66	2.71
0.5	0.75	10.71	2.87	2.09
0.5	0.95	11.37	2.68	1.78
0.75	0.25	7.76	5.76	2.25
0.75	0.5	8.84	4.57	2.27
0.75	0.75	9.84	3.56	2.24
0.75	1.0	10.43	2.54	2.47
0.75	1.25	6.33	2.59	1.85
1.0	0.25	7.69	6.0	2.15
1.0	0.5	7.87	4.77	2.77
1.0	0.75	8.54	2.63	3.62
1.0	1.0	9.9	2.56	2.79
1.0	1.25	11.28	2.34	2.05
1.25	1.5	11.38	2.42	1.93
1.25	0.25	6.25	4.71	3.84
1.25	0.5	8.28	4.26	2.82
1.25	1.25	9.55	2.63	2.98
1.5	0.25	6.38	4.74	3.75
1.5	0.5	7.19	4.19	3.56
1.5	0.75	8.44	3.59	3.11
1.25	1.5	10.08	1.98	3.02
2.0	0.25	6.83	4.98	3.31
2.0	0.5	7.64	4.57	3.04
2.0	0.75	8.59	4.1	2.71
2.0	1.0	8.23	3.16	3.5

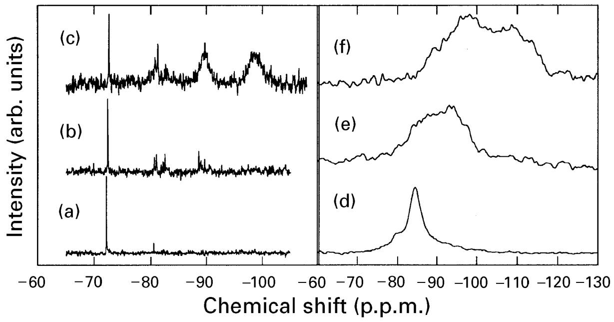

Figure 3 ^{29}Si NMR spectra of the type I products. Solutions (left side) and solids obtained by adding $CaSO_4$ (right side).
(a) $[SiO_2] = 0.105\ mol\,l^{-1}$, $[NaOH] = 0.7\ mol\,l^{-1}$,
(b) $[SiO_2] = 0.525\ mol\,l^{-1}$, $[NaOH] = 0.7\ mol\,l^{-1}$,
(c) $[SiO_2] = 1.05\ mol\,l^{-1}$, $[NaOH] = 0.7\ mol\,l^{-1}$,
(d) $[SiO_2] = 6.79\ mol\,g^{-1}$, $[Na_2O] = 1.43\ mmol\,g^{-1}$, $[CaO] = 4.46\ mol\,g^{-1}$,
(e) $[SiO_2] = 7.82\ mol\,g^{-1}$, $[Na_2O] = 2.57\ mmol\,g^{-1}$, $[CaO] = 22.2\ mol\,g^{-1}$,
(f) $[SiO_2] = 9.91\ mol\,g^{-1}$, $[Na_2O] = 2.27\ mmol\,g^{-1}$, $[CaO] = 0.8\ mol\,g^{-1}$.

entities and spectrum (f) shows the presence of Q^3 and Q^4 entities. It must be emphasized that spectrum (e) is that of a solid consisting of a silicate network which is plate like at the nanometer scale. Spectrum (f) is typical of a three dimensional amorphous silicate network.

These differences indicate the existence of a third domain on the ternary diagram. The borderline between these two domains is ill-defined but it is represented with a dashed line in Fig. 2.

To conclude, the degree of condensation of $[SiO_4]$ tetrahedra increases with increasing the proportion of silica in the solid. Natural silicates [8] show a similar behaviour. The alkali–silica solution spectra exhibit the same features as previously published spectra [5, 7]. A comparison of the solution and solid state spectra indicates that the solid seems in general, to be more polymerized than the solution.

3.2. The mean structure of the solid versus the mean structure of the solution

From these experimental spectra the Q^n distribution and the mean degree of connectivity [7], namely,

$$\bar{n} = \frac{\sum_n nQ^n}{\sum_n Q^n} \qquad (1)$$

can be deduced.

In Fig. 4 we show the mean degree of connectivity of the solid versus the mean degree of connectivity of the solution for the type I products. It can be seen on this curve that there is no significant difference between the solids obtained by $CaSO_4$ or by $CaCl_2$ action. To a first approximation the points are roughly spread around a straight line whose slope is 0.6 and whose intersection of the y-axis occurs at 1.8. This straight line shows that the degree of polymerization of the solution governs the degree of polymerization of the solid.

These features indicate that the mean degree of connectivity of the solid is greater than the mean degree of connectivity of the solution.

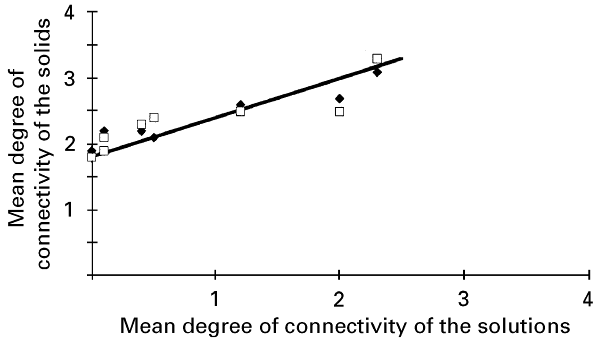

Figure 4 Mean degree of connectivity of the solid versus the mean degree of connectivity of the solution for the type I products. Key: (□) type I/$CaSO_4$ and (◆) type I/$CaCl_2$.

In particular, this indicates that a nano-crystalline chain-like calcium-silicate-hydrate can be obtained by interaction between calcium ions and a solution containing only monomers [9]. Moreover, a silicate solution containing entities up to Q^2 (or Q^3), may lead to a gel containing Q^3 (or Q^4) entities respectively.

3.3. Silicate species balance in the initial and final system

The curve in Fig. 4 shows an increased polymerization but it is constructed only with NMR data from only the initial solution and the solid obtained by calcium action. In fact, the system has three components and it is desirable to know how silicate ions are distributed amongst the whole system. With this aim in view, the distribution of the silicate species in the different components of the system before and after the addition of calcium ions was investigated. In order to have access to this structural and chemical distribution, the NMR and chemical data were combined.

The study has been conducted with two type II samples: one belonging to the precipitate domain and the other belonging to the gel domain.

The chemical analysis for the precipitate domain is presented in Table IV and for the gel domain in Table V. The NMR spectra shown in Fig. 5 are for the precipitate system and in Fig. 6 for the gel system. The results of the analysis of the NMR spectra are listed in Tables VI and VII.

Tables IV and V show that the balance sheet of K and Ca elements is correct for the precipitate system

TABLE IV Chemical analysis of the type II products for the initial and final systems (precipitate domain)

	Si (mmol)	K (mmol)	Ca (mmol)	Mass (g)
Initial solution	26	101	18	100
Residual solution	2	90	1.5	97.36
Dry precipitate	20	11	16	2.64
Residual solution plus dry precipitate	22	101	17.5	

TABLE V Chemical analysis of the type II products for the initial and final systems (gel domain)

	Si (mmol)	K (mmol)	Ca (mmol)	Mass (g)
Initial solution	114	114	18	100
Residual solution	64	72	2	94.35
Dry gel	56	32	14	5.65
Residual solution plus dry gel	120	104	16	

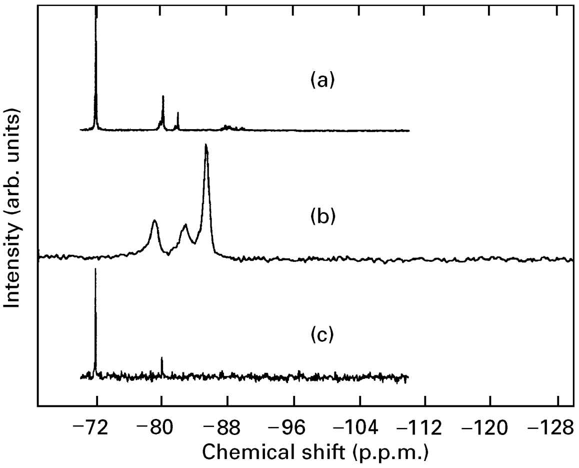

Figure 5 ^{29}Si NMR spectra for the precipitate system. (a) Spectrum of the initial solution, (b) spectrum of the precipitate, (c) spectrum of the residual solution.

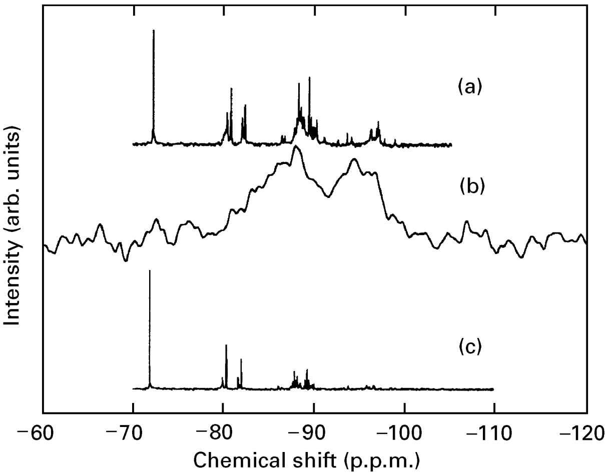

Figure 6 ^{29}Si NMR spectra for the gel system. (a) Spectrum of the initial solution, (b) spectrum of the gel, (c) spectrum of the residual solution.

but it is worse for the gel system (10% error); this arises due to the difficulty in separating the gel and the residual solution. The Si balance sheet is within 15% error and is affected by the imprecision of the silica content determinations involved in the chemical analysis.

Except for the solid gel, the NMR spectra are well resolved and integration is not difficult. Different attempts at the integration of the solid gel gave results comparable with those presented above.

TABLE VI Q^n analysis of the NMR spectra shown in Fig. 5

	Percentage of Q^0	Percentage of Q^1	Percentage of Q^2
Initial solution	56	28	7 $Q^{2\mathrm{Cy}}$ 9 $Q^{2\mathrm{lin}}$
Residual solution	82	18	0
Precipitate	0	24	76

TABLE VII Q^n analysis of the NMR spectra shown in Fig. 6

	Percentage of Q^0	Percentage of Q^1	Percentage of Q^2	Percentage of Q^3
Initial solution	9	14	7 $Q^{2\mathrm{Cy}}$ 56 $Q^{2\mathrm{lin}}$	14
Residual solution	21	20	11 $Q^{2\mathrm{Cy}}$ 40 $Q^{2\mathrm{lin}}$	8
Gel	0	0	57	43

TABLE VIII Silicate species balance in the initial and final system (precipitate domain)

	Percentage of Q^0 (mmol)	Percentage of Q^1 (mmol)	Percentage of Q^2 (mmol)
Initial solution	56	28	16
Residual solution	82	18	0
Precipitate	0	24	76

TABLE IX Silicate species balance in the initial and final system (gel domain)

	Percentage of Q^0 (mmol)	Percentage of Q^1 (mmol)	Percentage of Q^2 (mmol)	Percentage of Q^3 (mmol)
Initial solution	9	14	63	14
Residual solution	21	20	51	8
Gel	0	0	57	43

The number of moles of Si engaged in the different Q^n entities for each element taken in the precipitate domain and in the gel domain was determined. In order to achieve this aim, the product of the moles of Si in the constituent and of the Q^n quantity was calculated. Thus, the following calculations were made for each of the two systems;

(I) the number of moles of silica in the initial solution multiplied by the quantity of Q^n entities present in the medium,

(II) the number of moles of silica in the residual solution multiplied by the quantity of Q^n entities present in the medium, and

(III) the number of moles of silica in the solid multiplied by the quantity of Q^n entities present in the medium.

The results are listed in Tables VIII and IX and they are illustrated in the form of a histogram in Figs 7 and 8.

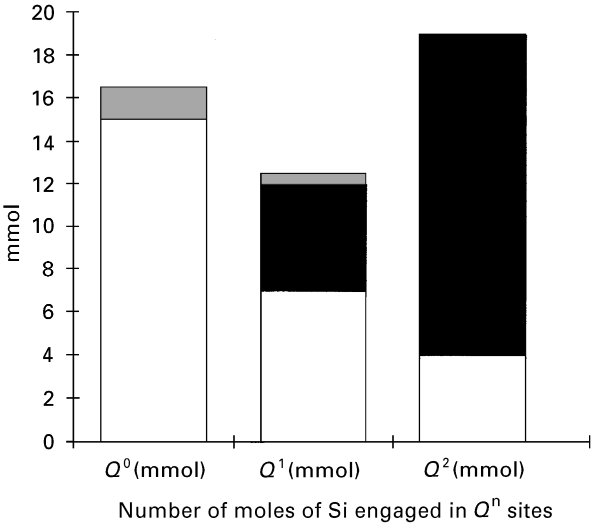

Figure 7 Histogram showing the silicate species balance in the initial and final system (precipitate domain). Key: (□) initial solution, (■) precipitate and (▨) residual solution.

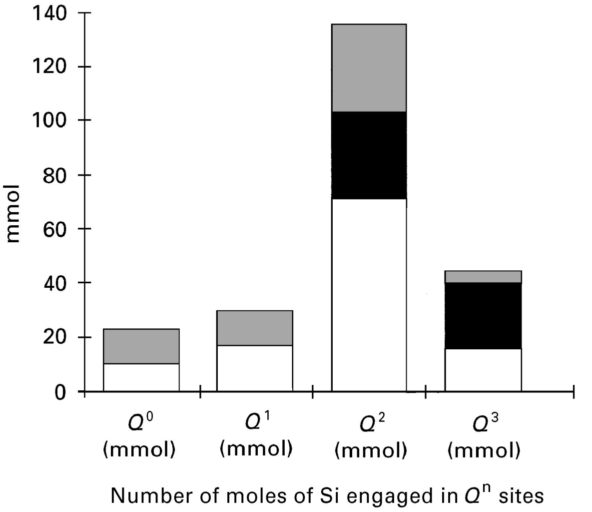

Figure 8 Histogram showing the silicate species balance in the initial and final system (gel domain). Key: (□) initial solution, (■) gel and (▨) residual solution.

3.3.1. Precipitate domain

It is noteworthy, that in the final system the more polymerized entities are located in the solid and the less polymerized ones in the residual solution.

The histogram shows a loss of Q^0 and Q^1 entities and an excess of Q^2 entities in the final (residual solution plus solid) system. The excess of Q^2 entities is more pronounced in the solid.

3.3.2. Gel domain

The highly-polymerized and lower-polymerized species distribution between the two components of the final system is the same as before.

The histogram shows an excess of Q^0 and of Q^3 entities and a loss for the other species in the final system. The excess of Q^0 entities in the residual solution is a sign of the return to equilibrium of the less silica-rich solution. The excess of Q^3 species is more important in the solid. Thus, coagulation of the polysilicate anions by calcium ions is accompanied by the condensation of the polysilicate anions.

In this domain, it has been observed that the mixing of calcium hydroxide and a potassium silicate solution exhibits the surprising behaviour of complete dissolution of the $Ca(OH)_2$ particles. The dissolution leads to a clear and fluid solution, similar to the one formed when Ca^{2+} ions are complexed with Ethylene Dinitrio Tetraacetic Acid (EDTA) in high pH media. This sol is metastable and transforms to a gel a few hours later. A ^{43}Ca NMR investigation has been conducted on the metastable sol and also on the gel [10]. This study has shown that the calcium has the same environment in the sol as in the gel. The calcium ion can not be removed from the alkaline–calcium–silicate hydrate, except by acid attack since the calcium ion belongs to the structure of the solid. Consequently, the calcium ion does not only act as a scavenger; it also modifies the equilibrium in order to induce condensation of the polysilicate anions and links the silicate species together. The structure of the solid is probably organized around the calcium ion. The residual solution is just an equilibrium alkali–silica solution.

4. Conclusion

For increasing relative concentrations of silica in the solid, there is a steady increase in the degree of condensation of $[SiO_4]$ tetrahedra from the chain-like silicates, to ternary silicate networks, and finally to quaternary silicate networks. As a consequence, the influence of the cations on the structure of the silicates and, in particular on the topology and on the conformation of their tetrahedral entities, decreases in the sequence from the monomeric silicates to the chain-like silicates, to ternary silicate networks, and to quaternary silicate networks.

The counter-ion of the calcium in the calcium compound has no influence on the polymerization. However the calcium ion does not only act as a bridge between silicate ions in solution. It also initiates the condensation of silicate ions in solution and links the silicate species in order to form a solid with a mean degree of connectivity higher than that of the initial solution. The structure of the solid is probably organized around the calcium ion.

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