

SOLID-LIQUID EQUILIBRIA IN K-C-S-H/H₂O SYSTEMS

R. Dron
Laboratoire Central des Ponts et Chaussées

F. Brivot
Laboratoire Central des Ponts et Chaussées,
58 Bd Lefèbvre, 75732 Paris cedex 15

ABSTRACT

The ASR products were synthesized by reaction *in vitro* of a constant amount of calcium hydroxide with various solutions for various concentrations of silica and potash.

According to the values of the two independent variables, the product obtained is either a precipitate exhibiting large similarities with C-S-H, but including strongly linked potassium, or an amorphous gel retaining almost all of the water of the initial solution.

The gel system is formed by coagulation of a calcium-silicate ionic complex appearing when high Si/K ratio was used. The solution of the complex is clear and fluid and is transformed into a gel within 24 hours.

It is shown that the whole system is divariant, that is to say that the ternary composition of the solid (precipitate or gel matrix) depends on two parameters, which are the final concentrations in the liquid (mother liquor or serum), in equilibrium with the solid.

The question of the composition of the ASR products has therefore not an unique answer but a double infinity, in a limited fields of the ternary system CaO-K₂O-SiO₂.

Keywords: composition, ASR product, pore solution, equilibrium diagram

INTRODUCTION

The characterization of the alkali-silica products by their C/S and K/C ratio (obtained for example by EDX) assumes that there is a well-defined composition that is the signature of this pathology. In fact, this idea runs up some difficulties of principle, related to the complexity of the matter in question (Davies & Oberholster 1988, Way & Shayan 1992)

The first difficulty lies in the fact that one is dealing not with a solid comparable to a mineral grain or a crystal, but with the result of drying of a product initially soaked with water like a sponge. This product is therefore two-phased, but the overlap of the phases, on a scale smaller than the resolving power of the SEM, is not accessible to observation. Moreover, the liquid phase never consists of pure water, but of a solution, sometimes a rather concentrated one. Its evaporation leaves a residue that throws off the composition of the underlying solid matter.

The second difficulty is related to the degree of complexity of the system, which includes four independent constituents (CaO, K₂O, SiO₂, H₂O). This notion introduces by an other way the consideration of the phases and their number. The phase rule can be used to answer this question, and also that of whether the composition is unique or not.

VARIANCE OF THE SYSTEM K-C-S-H/H₂O

Gibbs law or phase rule can be used to quantify the variance of a system in equilibrium :
 $V = C + 2 - \Phi$

The variance V is the number of intensive variables (pressure, temperature, local compositions) that can change independent of one another without the equilibrium being broken.

C is the number of independant constituents (here 4 as stated above).

Φ is the number of phases.

When the two physical intensive variables P and T are fixed, the relation becomes :

$$V = C - \Phi$$

that is to say, since $C = 4$

$$V = 4 - \Phi$$

Since the system includes, in addition to the liquid phase at least one solid phase, the variance cannot be greater than two. This means that two variables at most are sufficient to characterize the system. We have chosen the two concentrations of the liquid phase, respectively [K] and [SiO₂].

In fact, it is in the other direction $\Phi = 4 - V$ that we will be using the phase rule because it is easier to quantify the variance than to count the phases.

Since Φ is at least equal to 2, V can take only the values 2, 1 or 0.

- If the system is invariant, this means that all the variables, in particular [K] and [SiO₂], chosen as principal variables, have fixed values.
- If the system is monovariant, this means that [K] and [SiO₂] are correlated.
- If the system is bivariant, [K] and [SiO₂] are independent.

It follows clearly from our experiments that both concentrations [K] and [SiO₂] in fact vary, which rules out the first case, and that they are not correlated, which rules out the second. It follows that the system is bivariant, which implies the existence of only one solid phase. Its composition depends on the values of the two principal variables [K] and [SiO₂]. The purpose of the present work is to establish this relation and state it in the form of an equilibrium diagram.

EXPERIMENTAL PART

Leading idea

The main conclusion drawn from the researches we have conducted on the alkali-aggregate reaction is the existence of a mechanism acting via dissolution, in two main steps (Dron, Nonat & Brivot 1994)

In the course of the first step, the pore solution of the concrete, when made sufficiently alkaline by the alkalis from the cement, attacks the reactive silica, causing it to go into solution in the form of silicate ions, more or less polymerized and more or less electrically charged.

In the course of the the second step, the calcium hydroxide dissolves in the solution resulting of the first step, giving rise either to a precipitate when the silicate anions are only slightly polymerized and to a sol when they are more polymerized. The sol is unstable and then coagulates in the form of a gel. It is this second step that is accompanied by expansion (Dron & Brivot 1992-93, Nieto et al 1995).

The syntheses we performed skip the first step and simulate the second, by using slaked lime and potassium silicate solutions of varied concentrations and varied K/SiO₂ ratios as starting products.

The experience plane is based on the variation of the molarities by step of 0.25 mole kg⁻¹, respectively from 0 to 2 mole kg⁻¹ for K and from 0 to 1 mole kg⁻¹ for Si.

Synthesis procedures

The solutions are prepared by mixing the following reagents, in the desired proportions :

- a commercial potassium silicate solution (0.935 mole kg⁻¹ K₂O and 3.7 mole kg⁻¹ SiO₂), density 1.27
- a 2 mole kg⁻¹ potassium hydroxide solution produced by dissolving pellets in freshly boiled distilled water.
- the calculated quantity of boiled water.

These mixtures are prepared 3 days before use, to allow the depolymerization equilibrium to become established.

The reaction takes place in a 200 ml polyethylene vessel. A constant quantity of 1 g of quicklime is put into it, and 10 ml of hot water then added, to completely slake the lime. The solution to be tested is then added and agitated by a magnet. The vessel is then tightly closed and kept under agitation for 1 hour. After this time, the vessel is left at rest at least one week before the next operations are performed.

Type of products obtained

Depending on the composition of the starting solutions, the final product appears in one or the other of two very different forms :

- In a certain number of cases, corresponding to starting solutions having low silica concentrations, the product has the characteristics of a precipitate, which is deposited at the bottom of the container. The mother liquor is easily separated by simple filtration.
- For more concentrated starting solutions, the content of the vessel, initially milk-like, progressively clarifies, while the viscosity increases, and remains homogeneous when the agitation is stopped.

After a night rest, it is found that a coagulation has occurred, and all the liquid has turned into a translucent gelatinous mass. The phenomenon of syneresis is observed (spontaneous separation of small quantities of serum). Ultra-centrifugation is used to obtain a sufficient quantity for the analysis. The respective concentrations of K and SiO₂ are determined by potentiometric titration and emission spectrometry (ICP) on the mother liquor or serums immediately after their separation.

Before analysis, to eliminate the solution impregnating them, the solid products (precipitates and gels) must be washed in a way that does not affect their composition. A sample of approximately 10 g is triturated with 100 ml of water and immediately centrifuged, then washed a second time. Significant decomposition takes place only with contact of at least one hour. The analysis of Ca, Si and K is performed by ICP after drying, calcination, melting in lithium tetraborate, and dissolution in hydrochloric acid.

INTERPRETATION OF THE RESULTS

It appears clearly (Fig. 1) that the composition of the final liquid phase is variable, which means that the variance is not equal to zero.

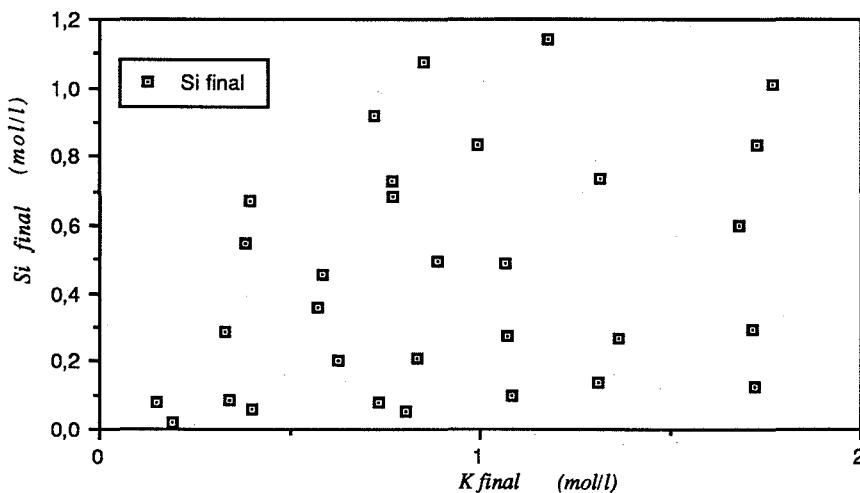


Fig. 1 : Composition variability of the liquid phase

Furthermore no correlation appears between the concentrations of $[K_2O]$ and $[SiO_2]$ which rules out the value one for the variance and leaves the value two as sole possibility. The system is therefore necessarily two-phased, i.e., since $\Phi = 4 - V$, only two phases (a liquid phase and a solid phase) occur in the system.

This conclusion makes it possible to predict the existence of a relation between the composition of the two phases (solid and liquid). The difficulty lies in the fact that both compositions are expressed by two parameters (but only two since for the solid, the CaO content is the complement to 100 of the K_2O and SiO_2 contents, expressed in mole percent of the anhydrous matter)

Graphic processing can overcome this difficulty : The composition of the solid is plotted on a ternary diagram. To each point is assigned the concentrations, of $[K]$ and $[SiO_2]$ of the corresponding solution. It is found that the iso concentrations $[K]$ lines are arranged parallel to the side of the triangle opposite to the K_2O apex.

In addition, the iso concentration $[SiO_2]$ lines are arranged radially around the pole having the composition $K_2O = 30\%$, $CaO = 30\%$, $SiO_2 = 40\%$ which appears as the limit towards which the composition tends for increasing concentrations $[K]$ and $[SiO_2]$ in the solution.

This led us to test the correlations that these qualitative characteristics implies. Hyperbolic forms seem appropriate to reflect the asymptotic effect at $K_2O = 30\%$, $SiO_2 = 40\%$

Isoconcentration lines for $[K]$:

They are at $K_2O = \text{constant}$, which means that there is a well defined value x of $[K]$ for any value X of K_2O

The form $x = AX/(30-X)$ takes into account the fact that the absence of K_2O in the solid implies its absence of K the liquid phase.

Fig. 2 shows that the correlation is significant ($R^2 = 0.829$) and gives the value $A = 0.6$

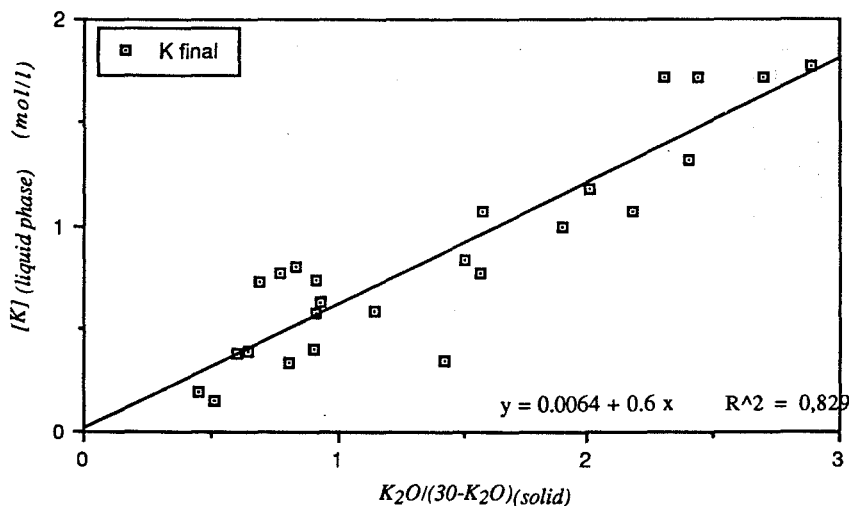


Fig. 2 : Test of the correlation $[K]$ (liquid phase) versus $K_2O/(30-K_2O)_{(solid)}$

Isoconcentration lines for $[\text{SiO}_2]$:

The straight lines that converge at the point $X=30, Y=40$ are characterized by their slope $p = (Y-40)/(X-30)$, which leads us to test the correlation $[\text{SiO}_2] = F(p)$.

Fig. 3 shows that this correlation is significant ($R^2 = 0.816$) and that it is expressed by the relation

$$[\text{SiO}_2] = 0.43 (\text{SiO}_2-40)/(30-\text{K}_2\text{O}) - 0,2$$

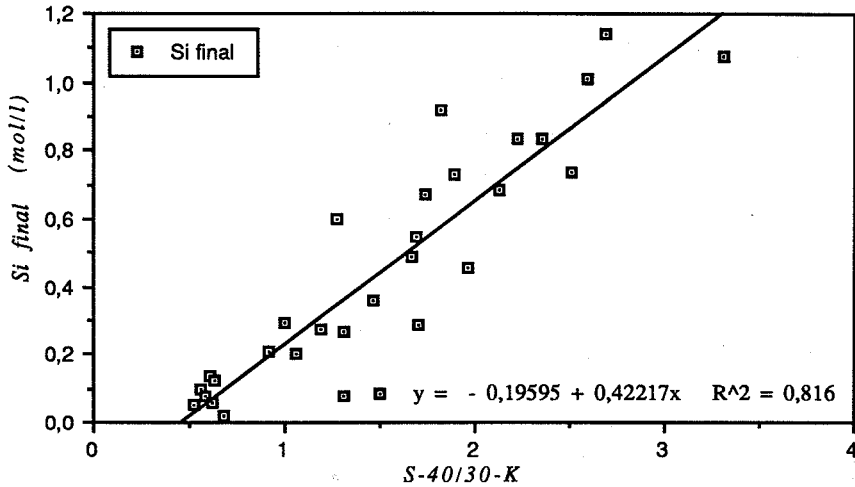


Fig. 3 : Test of the correlation $[\text{SiO}_2]$ (liquid phase) versus $(\text{SiO}_2-40)/(30-\text{K}_2\text{O})$ (solid)

The following numerical values can therefore be inferred

[K]	K_2O	$[\text{SiO}_2]$	SiO_2-40 $30-\text{K}_2\text{O}$
0	0	0	0.465
0.125	5.17	0.125	0.756
0.25	8.82	0.25	1.046
0.5	13.64	0.5	1.628
1	18.75	1	2.791
2	23.07		

PLOT OF THE EQUILIBRIUM DIAGRAM

The straight lines corresponding to the different values of the [K] and $[\text{SiO}_2]$ concentrations of the liquid phase are plotted on the $\text{K}_2\text{O} - \text{CaO} - \text{SiO}_2$ ternary molar composition diagram of the solid phase.

It results from the mathematical form of the expressions selected for [K] and $[\text{SiO}_2]$ that the lines of equal value of the ratios $[\text{K}] / [\text{SiO}_2]$ are straight lines that converge at the point having the co-ordinates $\text{K}_2\text{O} = 0$ $\text{CaO} = 46.05$ $\text{SiO}_2 = 53.95$ which corresponds approximately to the 6 CaO, 7 SiO_2 stoichiometry.

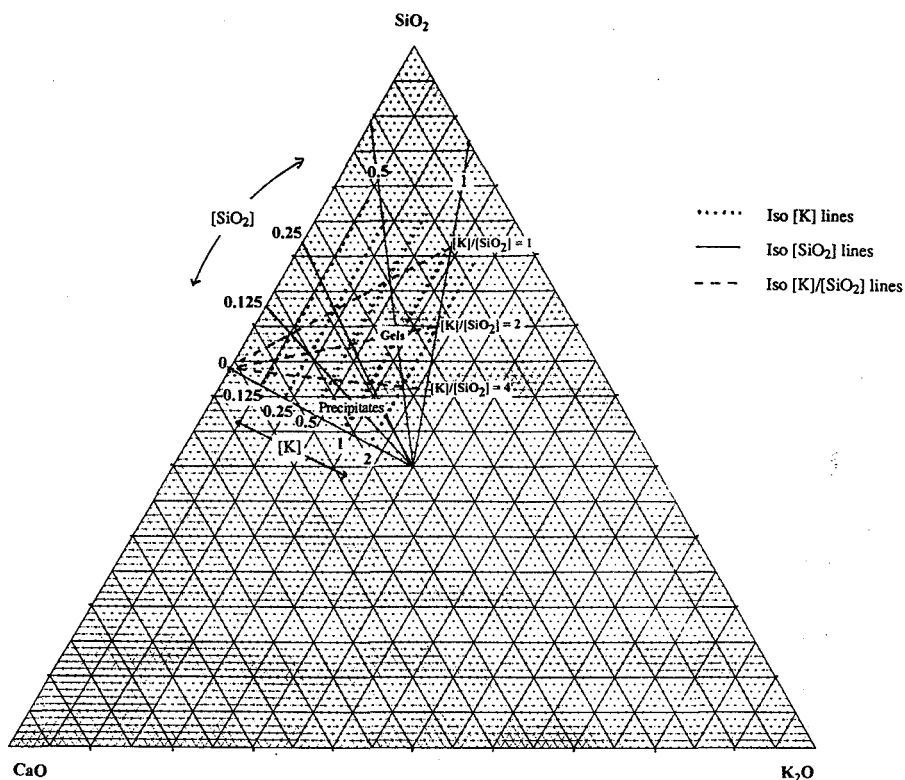


Fig. 4: Equilibrium diagram of the K-C-S-H / H₂O system

The useful part of the diagram is divided into two fields that correspond respectively to the precipitates and to the gels, with the extent of the domain of molar compositions of the solid phases being approximatively the following

	K ₂ O	CaO	SiO ₂	C/S
precipitates	10 - 25	30 - 37	45 - 55	0.6 - 0.7
gels	10 - 25	15 - 20	55 - 72	0.2 - 0.4

CONCLUSIONS

Processing of the analytical data of a large number of systems, obtained by synthesis in the system K-C-S-H + solution, established the relation, anticipated by the phase rule, between the composition of the solid phase and that of the liquid phase, and allowed it to be expressed in the form of an equilibrium diagram.

In triangular representation of the K₂O - CaO - SiO₂ ternary composition of the solid phases, the lines of equal concentration of the corresponding solutions can be regarded as straight lines, parallel to the side CaO-SiO₂ in the case of the iso [K] lines and convergent at the point of K₃C₃S₄ stoichiometry for the iso [SiO₂] lines. The lines of equal value of the ratio [K] / [SiO₂] converge at the point corresponding to the C₆S₇ stoichiometry.

From a practical viewpoint, the main thing this work has taught is that it is not possible to assume a unique composition of ASR products, but compositions vary rather considerably and depend on the composition of the final liquid phase.

To any pair $[K]$, $[SiO_2]$ of concentrations of potassium and silica of the final solution there corresponds a particular ternary composition of the solid matter in equilibrium with this solution.

- When the ratio $[K] / [SiO_2]$ is greater than 4, the solid appears in the form of a precipitate.
- When it is less than 4, the solid phase consists of a gel, as the term is understood in colloid chemistry.

The final value of the ratio $[K] / [SiO_2]$ is related to the initial chemical conditions (relative quantities of the reagents). In a system where the silica is consumed as it goes into solution, which is the case if transfers by diffusion are rapid and if the medium remains saturated in calcium hydroxide, this ratio tends to increase. Under these conditions, products of the precipitate type will form. In a system where the silica can accumulate locally because of diffusion barriers, gels will form.

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