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INVESTIGATION OF THE $CaO-Al_2O_3-SiO_2-H_2O$ SYSTEM AT 25°C BY THERMODYNAMIC CALCULATIONS

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ABSTRACT

The $CaO-Al_2O_3-SiO_2-H_2O$ system has been calculated at 25°C using new data on C-S-H and hydrogarnets. Thirty seven phase assemblages are found to be stable at this temperature. Despite the approximations made, the phase assemblages described are in accordance with most of the phase assemblages found experimentally for temperatures ranging from 25 to 85°C.

Introduction

High alumina cements may be blended with silica-containing compounds such as blast furnace slags (BFS), fly ashes (FA) or ordinary Portland cement. Thus silica becomes available in these systems and hydrates containing both alumina and silica may form: hydrogarnets ($C_3AS_xH_{6-2x}$) and gehlenite hydrate (C_2ASH_8). In order to define the stability field of these hydrates relative to C_3AH_6, the $CaO-Al_2O_3-SiO_2-H_2O$ system has been studied. In fact the conclusions can also be applied to glass cements (1) or metakaolin-calcium hydroxide systems (2). Due to the generally slow kinetics observed experimentally, it has been decided to study the $CaO-Al_2O_3-SiO_2-H_2O$ system by thermodynamic calculations as this method has proven to be reliable for other systems (3). This method enables us to define the stable phases and assemblages of the system. Dron (4) already used this technique to describe a simplified phase diagram for the $CaO-Al_2O_3-SiO_2-H_2O$ system. However in the work reported here, we have incorporated most recent findings to make it as accurate as possible even if the nature of hydrates such as C-S-H forces us to make some simplifications.

Method of calculation

First of all, the solid hydrates have to be added to the thermodynamic database associated with the computer program which determines their stability range. One of the main parameters of the database is the solubility product of the hydrates. The solubility products are generally calculated from experiments during which the solids are dissolved in pure water or more complex solutions. To be suitable, these experiments have to be carried out at constant temperature (the solubility product varies with temperature), without any atmospheric CO_2 contamination and the solid phase must be checked after the experiment to be sure that no transformation has occurred. Moreover, several redispersion steps are often needed to obtain reliable data. The values of the solubility product for the hydrates are not given here because they mainly depend on the method used to calculate it; equation of dissolution, method to calculate the activity coefficient... However the composition of the solution in equilibrium with each solid is given in table I. The reader can thereafter recalculate a solubility product if desired.

The $CaO-Al_2O_3-SiO_2-H_2O$ system contains two sub-systems; $CaO-Al_2O_3-H_2O$ and $CaO-SiO_2-H_2O$. The $CaO-Al_2O_3-H_2O$ sub-system has been calculated previously (3) and is not described again in this paper. Models for the $CaO-SiO_2-H_2O$ system have been reported previously (5,6) but none of these seem to be completely satisfactory. The calculation of the solubility product for C-S-H is problematic due to its variable composition (7) and its metastability relative to crystalline calcium silicate hydrates. Moreover recent works (8-10) tend to indicate that at least two different kinds of C-S-H exist. C-S-H(SI) with a low C/S ratio would be stable in solution having lime concentrations lower than 20mmol/l (9,10). On the contrary, C-S-H(SII) has a higher C/S ratio and would be stable in solutions with lime concentrations greater than 20mmol/l (9,10). Even if pure C-S-H(SI) and C-S-H(SII) can be synthesised (11) their solubilities in various lime solutions have not been determined yet. From a survey of the literature data, two solubility curves for C-S-H have been proposed (12). We do not agree that the literature data fall onto two curves, but instead scatter. Moreover the two solubility curves never cross (12) and as a consequence, C-S-H having the upper solubility curve is always metastable with respect to C-S-H having the lower solubility curve. In the model for the $CaO-SiO_2-H_2O$ system presented here, two C-S-H's, each with a define stability range have been considered:

- C-S-H(SI) for lime concentrations below 20mmol/l. Its C/S is considered to be constant at an average value of 1.1
- C-S-H(SII) for lime concentrations above 20mmol/l. Its C/S is constant and equal to 1.8
- C-S-H(SI) and C-S-H(SII) are in equilibrium at a lime concentration equal to 20mmol/l.

Of course this model does not take into account the most stable phases for the $CaO-SiO_2-H_2O$ system but it is nevertheless of interest due to the time involved in the transformation of the C-S-H into more stable phases such as tobermorite. The value of the solubility product of C-S-H(SI) has been calculated as an average value from experimental data on the $CaO-SiO_2-H_2O$ system (13-15). However for C-S-H(SII) the solubility product has been calculated from the invariant point C-S-H(SI)+C-S-H(SII); the composition of the solution at this point correponds to the silicate concentration of the equilibrium curve of C-S-H(SI) at a lime concentration of 20mmol/l. Moreover the incorporation of Al_2O_3 into C-S-H was not taken into account even though the C/A ratio of C-S-H can be significant (16). In this paper, our attention is mainly focused on phases containing essential alumina so the specific approximations made for the $CaO-SiO_2-H_2O$ system are not crucial.

The quaternary hydrates, hydrogarnet and gehlenite hydrate, must also be added to the hydrates of the two previous sub-systems. Jappy (17,18) has demonstrated that a complete solid solution between C_3AH_6 and C_3AS_3 (grossular) does not exist, as was postulated before (19). Roy and Roy (20) also reported miscibility gaps at much higher temperatures. For temperatures lower than 100°C, it seems that two series of hydrogarnet exist; a low SiO_2 containing hydrogarnet (HG Si low) and a higher SiO_2 containing hydrogarnet (HG Si high). However the range of SiO_2 content of these two series varies with temperature. In the results presented here, we have used two hydrogarnets with a constant SiO_2 content representative of the two series:

- HG Si low: $C_3AS_xH_{6-2x}$ with $0.2<x<0.4$ and x fixed at 0.3 in the calculations
- HG Si high: $C_3AS_xH_{6-2x}$ with $0.6<x<1.0$ and x fixed at 0.8 in the calculations.

In Jappy's experiments (17), hydrogarnets of each series were never synthesised in pure phase form; mixtures of the two occurred. The solubility product has been calculated from these mixtures considering that the two phases were in equilibrium with the solution (invariant point). The data used to calculated the solubility product for gehlenite and the two hydrogarnets are summarised in (21). The computer program used to calculate equilibrium is derived from PHREEQE (22). Activity coefficients are calculated using Pitzer's relations (23).

TABLE 1

Calculated Composition of the Solution in Equilibrium with the Solid Dissolved In Water at 25°C

	[Ca] mmol/kg	[Al] mmol/kg	[Si] mmol/kg	pH
C-S-H(SI)	1.228		1.116	11.03
C-S-H(SII)	5.212		2.895	11.69
SH amorphous			1.413	6.37
C_2ASH_8	0.769	0.769	0.384	10.59
HG Si low	2.926	1.951	0.292	11.49
HG Si high	2.207	1.472	0.588	11.29
C_3AH_6	3.711	2.474		11.64
CH	21.95			12.54
AH_3 (gibbsite)		3.25e-6		6.99

Results

The $CaO-SiO_2-H_2O$ system at 25°C

The calculated phase diagram is shown as figure 1. Three phase assemblages have been found stable: SH + C-S-H(SI) + aqueous phase (aq), C-S-H(SI) + C-S-H(SII) + aq, C-S-H(SII) + CH + aq. (point on figure 1). C-S-H(SI) is stable over wide silicate concentrations, from 3.38e-5 to 5.24e-3mol/kg (table 2). However C-S-H(SII) only coexists with very low silicate concentrations. As it can be understood from figure 1, it seems to be difficult to differentiate experimentally the equilibrium curve of C-S-H(SII) from the equilibrium curve of C-S-H(SI).

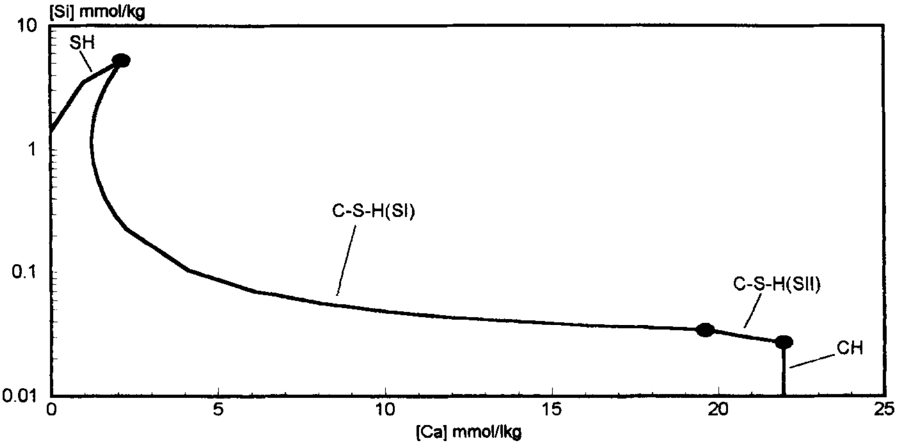

FIG. 1. Phase Diagram of the $CaO-SiO_2-H_2O$ System at 25°C

TABLE 2
Calculated Composition of the Aqueous Phase at the Invariant Points of the $CaO\text{-}SiO_2\text{-}H_2O$ System at 25°C (aq. = aqueous phase)

Invariant point	[Ca]mol/kg	[Si] mol/kg	pH
SH + C-S-H(SI) + aq.	2.137e-3	5.244e-3	10.30
C-S-H(SI) + C-S-H(SII) + aq.	1.960e-2	3.379e-5	12.48
C-S-H(SII) + CH + aq.	2.196e-2	2.704e-5	12.52

The $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$ system at 25°C

The phase diagram appears to be complex (FIG. 2); 9 hydrates are stable and have a surface of equilibrium in the phase diagram at 25°C. The intersections of these surfaces of equilibrium define 10 phase assemblages corresponding to 10 invariant points:

- AH_3 + HG Si low + C_2ASH_8 + aq.
- AH_3 + C-S-H(SI) + C_2ASH_8 + aq.
- AH_3 + HG Si low + C_3AH_6 + aq.
- AH_3 + C-S-H (SI) + SH + aq.
- CH + C_3AH_6 + HG Si low + aq.
- CH + C-S-H(SII) + HG Si low + aq.
- HG Si low + HG Si high + C_2ASH_8 + aq.
- HG Si high + C_2ASH_8 + C-S-H(SI) + aq.
- HG Si high + HG Si low + C-S-H(SI) + aq.
- HG Si low + C-S-H(SI) + C-S-H(SII) + aq.

The composition of the solution at these invariant point is given in table 3. Eighteen compatible phase assemblages corresponding to 18 boundary curves can also be determined from the phase diagram at 25°C:

- CH + C_3AH_6 + aq.
- CH + HG Si low + aq.
- CH + C-S-H(SI) + aq.
- C-S-H(SI) + HG Si low + aq.
- C-S-H(SI) + C-S-H(SII) + aq.
- C-S-H(SI) + HG Si low + aq.
- HG Si low + HG Si high + aq.
- HG SI low + C_2ASH_8 + aq.
- C_3AH_6 + AH_3 + aq.
- C-S-H(SI) + SI HG low + Si HG high + aq.
- C_3AH_6 + HG Si low + aq.
- C-S-H(SI) + HG Si high + aq.
- HG Si high + C_2ASH_8 + aq.
- C-S-H(SI) + C_2ASH_8 + aq.
- AH_3 + C_2ASH_8 + aq.
- AH_3 + C-S-H(SI) + aq.
- SH + C-S-H(SI) + aq.
- AH_3 + SH + aq.

TABLE 3
Calculated Composition of the Aqueous Phase at the Invariant Points of the $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$ System at 25°C

Invariant Point	[Ca] mol/kg	[Al] mol/kg	[Si] mol/kg	pH
AH_3 + HG Si low + C_2ASH_8 + aq.	4.87e-3	3.02e-4	2.05e-5	11.91
AH_3 + C-S-H(SI) + C_2ASH_8 + aq.	2.77e-3	1.66e-4	1.70e-4	11.66
AH_3 + HG Si low + C_3AH_6 + aq.	5.61e-3	3.47e-4	6.30e-7	11.97
AH_3 + C-S-H (SI) + SH + aq.	2.14e-3	7.19e-6	5.24e-3	10.30
CH + C_3AH_6 + HG Si low + aq.	2.19e-2	7.59e-6	1.16e-5	12.52
CH + C-S-H(SII) + HG Si low + aq.	2.19e-6	6.68e-6	2.70e-5	12.52
HG Si low + HG Si high + C_2ASH_8 + aq.	5.32e-3	2.17e-4	3.51e-5	11.95
HG Si high + C_2ASH_8 + C-S-H(SI) + aq.	5.60e-3	1.43e-4	7.62e-5	11.97
HG Si high + HG Si low + C-S-H(SI) + aq.	7.04e-3	9.40e-5	6.24e-5	12.07
HG Si low + C-S-H(SI) + C-S-H(SII) + aq.	1.96e-2	8.28e-6	3.37e-5	12.48

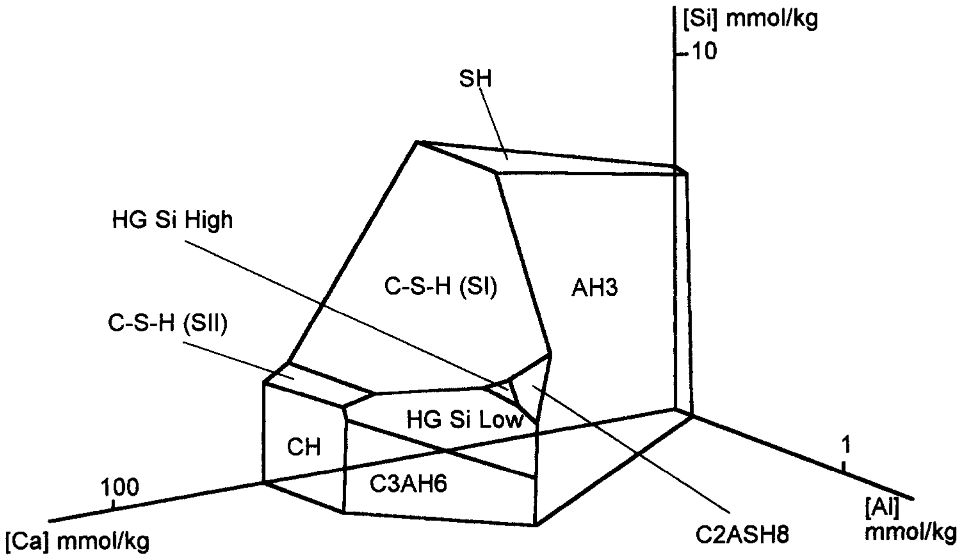

FIG. 2. Phase diagram of the $CaO-Al_2O_3-SiO_2-H_2O$ system at 25°C. The composition scale is non-linear: $\sqrt[5]{\text{concentration}}$.

Discussion

In the $CaO-Al_2O_3-SiO_2-H_2O$ system at 25°C, 37 phases assemblages coexist with the aqueous phase depending on its composition: 10 invariant points, 18 boundary curves and 9 hydrates. This enables us to understand why experiments often lead to different phase assemblages and apparently contradictory conclusions. Moreover the phase diagram indicates that small changes in the bulk composition can lead to drastic changes in the phases obtained. For example, it can be seen that C_2ASH_8 can be in equilibrium with either HG Si low or HG Si high or AH_3 or C-S-H(SI) with nearly the same aqueous phase composition. In addition, the existence of some phase assemblages rules out the existence of others: for example, if the assemblages CH + Si Hg low + C-S-H and CH + C_3AH_6 + Si Hg low + aq are stable, it is impossible to have the phase assemblage CH + C_3AH_6 + C-S-H + aq stable. In a similar manner, CH + Si HG low + Si HG high + aq found experimentally by Jappy (17) must be metastable because CH + Si Hg low + C-S-H + aq and Si Hg low + Si Hg high + C-S-H + aq are stable. The phase diagram also confirms that C_2ASH_8 is not stable in presence of CH: Locher (24) has observed that C_2ASH_8 + CH reacts giving mainly hydrogarnet.

Six invariant points out of the ten defined by calculation have been determined experimentally (table 4). Nine phase assemblages found experimentally also correspond to 9 boundary curves. These experimental results, even if they are collected from experiments carried out between 25 and 85°C, are consistent with our calculations at 25°C. This also indicates that the phase diagram does not change much between 25 and 85°C: the variation of solubility products with temperature only seems to modify the positions of the surfaces of equilibrium of the hydrates but does not either induce new phases or destabilise others. However this rule-of-thumb does not seem to be applicable for temperatures higher than 85°C above which:

- C_2ASH_8 is no longer stable
- C-S-H is transformed into crystallised calcium silicate hydrates
- zeolite-type compounds such as gismondine (2) and phillipsite may occur.

As a consequence the phase diagram is expected to be quite different at high temperatures.

TABLE 4
Phase Assemblages Found Experimentally for Experiments Carried out at Temperatures between 25 and 85°C

Phases assemblages for temperatures below 85°C	Reference
HG Si low + C-S-H(SII) + CH + aq.	2
HG Si high + C-S-H(SI) + C_2ASH_8 + aq.	2,25
AH_3 + C_2ASH_8 + HG Si low + aq.	27
C_3AH_6 + HG Si low + CH + aq.	17
HG Si low + HG Si high + C-S-H + aq.	17
AH_3 + HG Si low + C_3AH_6 + aq.	17
HG Si low + CH + aq.	17
C_2ASH_8 + C-S-H(SI) + aq.	2,26,27,28,29,30
HG + C-S-H + aq.	26,28
C_3AH_6 + HG Si low + aq.	28
C_2ASH_8 + HG Si + aq.	1
C_3AH_6 + CH + aq.	31
C_3AH_6 + AH_3 + aq.	31
CH + C-S-H + aq.	13,14,15
SH + C-S-H + aq.	13,14,15

The phase diagram may also be modified by additional components such as alkalies. As explained in previous calculations of phase diagrams (3), the introduction of moderate amounts of Na_2O shifts the surface of equilibrium of the hydrates and thus modifies the shape of the phase diagram. Moreover zeolites may form in presence of alkalies and as a consequence may complicate the phase diagram. Thus a better knowledge of zeolites that may form at low temperatures is required before investigating of the $CaO-Al_2O_3-SiO_2-Na_2O-K_2O-H_2O$ system.

Conclusions

Despite approximations made concerning C-S-H and hydrogarnet, the phase assemblages described from the calculated phase diagram are in good accordance with most of the phase assemblages found experimentally. The phase diagram enables us to define 37 phase assemblages that may explain some of the 'apparent' disagreement in the literature. But perhaps more important, addition of SiO_2 to the $CaO-Al_2O_3-H_2O$ system indicates that C_2ASH_8 and $C_3AS_x H_{6-2x}$ may form instead of C_3AH_6 and thus can lead to very different properties of the cementitious system: for example, with respect to durability.

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