CEMENTITIOUS PHASES

In the context of waste confinement and, more specifically, waste from the nuclear industry, concrete is used both as a confinement and a building material. High-level long lived radwaste and some of the intermediate level wastes are exothermic (e.g. compacted hulls and endspecies) and then, temperature exposure of concrete backfill and packages must be considered. The present work aims at defining the solubility constants of the minerals that compose cement pastes, based on the most recent works on this subject and in agreement with the Thermochimie data base. Data selection takes into consideration a range of temperatures from 10 to 100°C. This implies to develop a thermodynamic database complete enough in terms of mineral phases. This also implies to focus the selection not only on the equilibrium constants but on the enthalpy of formation and the heat capacity of each mineral. The chemical system investigated is a complex one, $CaO-SiO_2-Al_2O_3-MgO-Fe_2O_3-CO_2-SO_3-Cl-H_2O$. This includes nanocrystalline and crystalline C-S-H phases and accessory cementitious mineral such as ettringite or katoite, for example.

In summary, a solubility model for cement phases is proposed in Thermochimie because:

- cement is a key material for containment barriers

- available models still carry on problems concerning katoite, monosulfoaluminates

- available models are not consistent with Thermochimie

1 PRELIMINARY ASPECTS OF THE SELECTION PROCEDURE

1.1 SELECTION GUIDELINES

The selection for thermodynamic properties of cementitious minerals is proceeds following different guidelines :

- when possible, we avoid fitting LogK(T) functions, as well as averaging equilibrium constants. The aim is to avoid producing some new and perhaps confusing data

- when possible, LogK(T) function are calculated by using calorimetric data and compared to the results of solution equilibria in order to get a comparison involving different experimental technics

- solution equilibria results are selected according to the electroneutrality condition, the duration of the experiment, the analysis of final solid products and the experimental protocol

- equilibrium constants extracted from solution equilibria are recalculated by using the Thermochimie Database

- the selection is finally verified by drawing activity diagrams involving the minerals of interest in the chemical sub systems of concern.

The primary species for expressing equilibria in aqueous solutions are Al^{+++}, Ca^{++}, H_4SiO_4, Ca^{++}, Mg^{++}, Fe^{+++}, CO_3^{--}, Cl^-, SO_4^{--}, H_2O and H^+. The convention used to define the standard state of the compounds in the present work, is that proposed by Helgeson et al. (1981). Mineral/solution equilibria are calculated using the PHREEQC (Parkhurst and Appelo, 1999) and GWB software (Bethke 2006), and the extended Debye-Hückel activity coefficient correction model included in the Thermochimie database.

In addition, we have adopted a convention widely used for cementitious materials. We have used the following notations to designate chemical formula of minerals:

$C = CaO$; $S = SiO_2$; $A = Al_2O_3$, $M = MgO$, $F = Fe_2O_3$ and $H = H_2O$.

1.2 EXISTING SOLUBILITY MODELS, DATABASES AND CONSISTENCY ISSUES

Different works had been published to date concerning either the solubility of cementitious phases (see for example the case of ettringite, Myneni et al. 1998, Perkins and Palmer 1999) or phase relations for some more complex mineralogical assemblages (Ghorab et al. 1998a and b). Recently, an important work by Matschei et al. (2007) had provided new solubility data for a large set of minerals belonging to the cementitious chemical system. Based on those experiments, Lothenbach et al. (2008) have proposed their own solubility model for cement phases. It had been published after the project starting and remains the most complete to date. Further on in the text, we will see that their model may be discussed, concerning monosulfoaluminate and katoite, namely. We may also cite the solubility model developed by Thomas et al. (2003a) and based on a simplified mineralogy, since only the portlandite, gypsum, ettringite and monosulfate phases are considered.

The solubility of C-S-H has been specifically investigated by many authors. Among all of the solubility models published to date for nanocrystalline C-S-H, two large families may be distinguished: those for which the C-S-H are present as fixed-composition phases (Glasser et al., 1987) and those for which the C-S-H are considered as phases with a continually variable composition (Jennings 1986, Berner 1990, Kersten 1996). The influence of temperature is not taken into account in this type of model. Even for crystalline C-S-H, little solubility data is available beyond 25°C.

Recently, Damidot et al. (2011) have compared the present database and those compiled by Lothenbach et al. (2008). They found no major differences excepted for hydrogarnet and monosulfate. A brief discussion on this topic is given in conclusion of the present document.

2 DEVELOPMENT OF THE CEMENTITIOUS MODEL: THE CAO-SIO2-H2O SYSTEM

C-S-H are the mineral phases that give to the cement the main part of its compressive strength. They are formed by hydration of the C3S and C2S phases or during pozzolanic reactions with free lime. Crystalline C-S-H appears when high temperatures enhance crystallization (Atkins et al., 1994). At room temperature, the polymerization of tetrahedral SiO2 is less efficient, C-S-H appear initially as dimers then pentamers (Thomas et al. 2003b, Chen et al. 2004), as polymerization goes on.

2.1 CRYSTALLINE PHASES

Field observations are also of use in order to determine the stable character of C-S-H phases. In that case, the equilibration time represents hundreds of thousands of years whereas, in most cases, equilibration experiments last around several weeks or months. It may consequently be assumed that the minerals observed in natural contexts correspond to thermodynamically stable phases. Those include jennite and tobermorite (Smellie, 2000), observed as fracture infilling on several samples from the Maqarin site (Jordan). This is also the case for jennite and afwillite, which appear as fracture infilling in the Fuka skarn zone (Okayama prefecture, Japan, Kusachi et al. 1989). In this latter case, jennite seems to have precipitated at lower temperature, probably from the alteration of afwillite. Moreover, gyrolite and okenite are usually found associated with low temperature zeolites like apophyllite (Sukheswala et al., 1974), itself related to chabazite (Keith et al., 1985). Chabazite precipitates at temperatures ranging between 0 and 135°C, according to Rançon (1985). These observations would restrain gyrolite and okenite to low temperature domains. Xonotlite is observed associated with natrolite (Rogers et al., 2006). According to Rançon (1985), this would imply a temperature of formation ranging between 100 to 250°C. Similarly, Bargar et al. (1987) have identified truscottite related to laumontite, which requires a higher formation temperature between 180 and 300°C (Rançon, 1985). Concerning Hillebrandite and foshagite, these minerals have been observed in natural samples of the Bushveld skarn formation by Buick et al. (2000). Jaffeite (C6S2H3) has finally been determined in some Namibian samples by Sarp and Peacor (1989).

In conclusion, we can consider as thermodynamically stable the following minerals: jaffeite, hillebrandite, afwillite, jennite, xonotlite, foshagite, tobermorite, gyrolite and okenite. Among these, afwillite, jennite, gyrolite and okenite should be restricted to low temperature domains.The name and the structural formula of the main crystalline C-S-H are reported in Table 1.

2.1.1 Available thermodynamic data

Few calorimetric measurements are available to date for C-S-H. Thus, estimates from Babushkin et al. (1985) are widely used. Among the few calorimetric data available for C-S-H, Newman (1956) have measured the enthalpies of formation of hillebrandite, xonotlite and foshagite (34.7, 94.6 and 92.6 kcal/mol respectively), from the constituent oxides. For tobermorite 11A, Savage et al. (2007) collected the enthalpies of formation available throughout the literature. These authors report 3 measured values from Taylor (1968) with a mean discrepancy of 70 kJ/mol with respect to Babushkin et al. (1985) estimate. On the other hand, with the measurements from Zuern and Fehr (2000), the discrepancy is only 3.5 kJ/mol. We finally have retained the value provided by Zuern and Fehr (2000).

2.1.2   Refinement of the phase diagram for crystalline C-S-H

Phase transition have been refined in for crystalline C-S-H by using constraints issued from a bibliographic review that provides transition temperature for some mineral assemblages. In addition, we have calculated a linear relation between Babushkin et al. (1985) estimates of S° and Cp(25°C): Cp(25°C) = 1.15 * $S°_{Pr,Tr}$ - 28.39, where R² = 0.993. Finally, we have used the enthalpies of formation previously selected for tobermorite-11Å, hillebrandite, xonotlite and foshagite.

The results are given in Table 1, and are displayed in Figure 1. The latter indicates that the stable phases at 25°C are jennite, tobermorite-14A, hillebrandite and gyrolite. As the temperature increases, gyrolite and hillebrandite remain stable and afwillite, tobermorite-11A then xonotlite appear successively. The previous discrepancies in phase relations with the literature review do no longer appear. It is interesting to verify that jennite can actually be a part of the thermodynamically stable phases in the CaO-SiO2-H2O system. This point was not obvious before this calculation since our only temperature constraint for jennite consists in an inequality. On the other hand, foshagite disappears from the list of stable minerals. It is possible that 170°C for the afwillite-hillebrandite-foshagite assemblage is a somewhat low temperature; Speakman (1968), for example, have obtained foshagite only from 259°C. Finally, the refinement allow to a close agreement with constraints from literature review, even if results are less clear for foshagite.
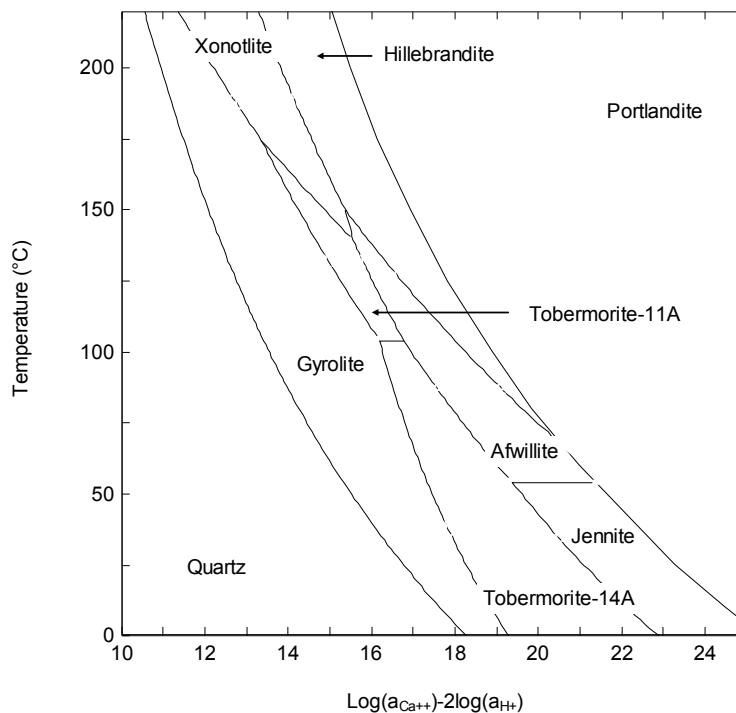

Figure 1   Phase diagram in the CaO-SiO$_2$-H$_2$O system, thermodynamic properties refined in this work

Table 1   *Thermodynamic properties of C-S-H phases, selected or calculated in this work*

Name	Formula	Log K(298)	$\Delta G^0{}_{f,298}$ kJ.mol^{-1}	$\Delta H^0{}_{f,298}$ kJ.mol^{-1}	$S^0{}_{f,298}$ J.mol^{-1}.K^{-1}	$Cp°_{298}$ J.mol^{-1}.K^{-1}	$V°$ cm^3.mol^{-1}
Crystalline C–S–H							
gyrolite	$Ca_2Si_3O_{7.5}(OH):2H_2O$	22.34b	-4550.06	-4917.99b	309.32	325.94b	137.34e
xonotlite	$Ca_6Si_6O_{17}(OH)_2$	91.34b	-9465.12	-10022.15b	573.74	628.64b	256.90e
tobermorite-14A	$Ca_5Si_6O_{16.5}(OH):10H_2O$	62.94b	-11090.12	-12175.15b	874.57	973.53b	351.30e
tobermorite-11A	$Ca_5Si_6O_{16.5}(OH):5H_2O$	65.58b	-9889.25	-10680.92b	692.55	764.91b	286.19e
foshagite	$Ca_4Si_3O_9(OH)_2:0.5H_2O$	65.96b	-5643.83	-6032.43b	295.07	309.38b	160.66e
jennite	$Ca_9Si_6O_{16}(OH)_{10}:6(H_2O)$	147.33b	-13886.77	-15189.04b	839.25	933.21b	456.40e
afwillite	$Ca_3Si_2O_4(OH)_6$	49.42b	-4469.06	-4853.82b	289.70	303.55b	129.53e
hillebrandite	$Ca_2SiO_3(OH)_2:0.17H_2O$	36.95b	-2481.95	-2662.48b	179.71	177.46b	72.58e
truscottite	$Ca_7Si_{12}O_{29}(OH)_4.H_2O$	77.08	-15280.40d	-16854.62d	927.68	1034.10d	478.73e
okenite	$CaSi_2O_{5}:2H_2O$	9.18	-2881.72d	-3135.70d	208.52	210.07d	94.77e
C_2SH,α	$Ca_2(HSiO_4)(OH)$	35.54	-2449.12d	-2634.92d	122.38	111.88d	71.12e
jaffeite	$Ca_6(Si_2O_7)(OH)_6$	114.06	-6469.94d	-6972.77d	326.19	344.90d	174.38e
Nanocrystalline C-S-H							
C-S-H1.6	$Ca_{1.6}SiO_{3.6}:2.58H_2O$	29.27a (1.67 Ca) 28.00c	-2550.86	-2819.79d	154.42	190.10d	84.68e
C-S-H1.2	$Ca_{1.2}SiO_{3.2}:2.06H_2O$	19.30c	-2161.23	-2384.34d	129.14	162.13d	71.95e
C-S-H0.8	$Ca_{0.8}SiO_{2.8}:1.54H_2O$	11.20a (0.83 Ca) 11.05c	-1769.03	-1945.13d	107.85	138.38d	59.29e

(a) Lothenbach et al. (2008) ; (b) Crystalline C-S-H phase diagram refinement ; (c) nanocrystalline C-S-H solubility refinement ; (d) calculated with the polyhedral model ; (e) literature review detailed in Blanc et al (2010a)

When no letter is associated, the numbers are internally calculated (e.g. gyrolite entropy is obtained by using its LogK$_{298}$ and its $\Delta H^0{}_{f,298}$).

2.2 NANOCRYSTALLINE C-S-H PHASES

Nanocrystalline C-S-H constitutes about 2/3 in weight of a cement paste hydrated at ambient temperature. The C/S ratios of these phases are variable, usually from 0.8 to 1.8 (Glasser and Atkins 1994, Berner 1990, Bennet et al. 1992, and Atkins et al. 1994). Atkins et al. (1994) report a limit temperature of 120°C for the observation of the gel phase, depending on kinetic constraints.

Among all of the various models published to date that take account of the solubility of such phases, two main families may be distinguished, C-S-H phases being considered either as discrete composition phases (Glasser et al., 1987) or with a continuously variable composition (Jennings 1986, Berner 1990, Kersten 1996). This type of model may be integrated in most of the geochemical codes able to manage solid solutions, but the major disadvantage is an increase of the computation time, or even the appearance of instabilities, particularly for reactive transport calculations. On the other hand, Stronach and Glasser (1997) and Courault (2000), have developed a 3 phases model: C/S=0.8 ; 1.1 and 1.8. Following these authors, given the crystallographic constraints, we have retained a 3-phase model, consistent with the review of Bourbon et al. (2001). Since there is no precise agreement on the composition, we have calculated the C/S ratios of these phases from the solubility data collected in the literature.

2.2.1 Solubility

In order to estimate the composition and the solubility of three C-S-H phases, we have collected a certain number of experimental works that provide the composition of the solution equilibrated with C-S-H phases. The collected data are shown in Figure 2. From these data, we have obtained the composition of three C-S-H phases: C/S = 1.6 ± 0.10 ; 1.2 ± 0.18 and 0.8 ± 0.16. The two latter values are close to the values retained by Stronach and Glasser (1997) and Courault (2000). Experimental gathered data are fitted through a least-squared process, leading to the following Log K values:

- C-S-H1.6: LogK = 28.00
- C-S-H1.2: LogK = 19.30
- C-S-H0.8: LogK = 11.05
- Portlandite : LogK = 22.81

The latter value is identical to the 22.81±0.4 value provided by Reardon (1990)[58] and Glasser et al. (2001) and it is also close to the value of 22.80 found by Humel et al. (2002) and Nordstrom et al. (1990). Figure 2 compares the results obtained with respect to experimental data. However, the experimental dataset is not exhaustive, namely with respect to the most recent works. In addition, we could calculate that an ideal solid solution based on C-S-H0.8 and 1.6 end members could provide a reasonable agreement, too, given the large dispersion of experimental data.
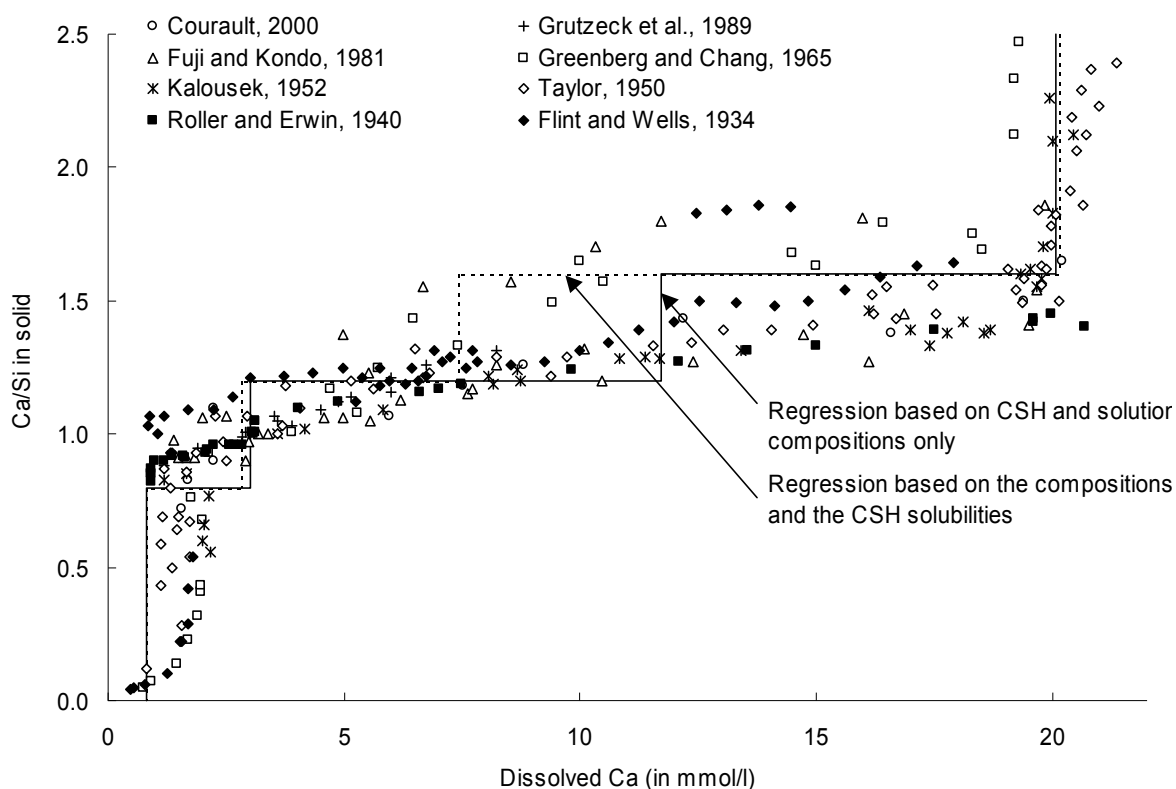
Figure 2   *Relation between C/S in C-S-H and dissolved calcium concentration, according to different authors*

2.2.2   Polyhedral model

Despite a close examination of the available literature, we are lacking the enthalpy of formation and the heat capacity of nanocrystalline C-S-H. In addition, the thermodynamic properties of some important phases such as okenite, jaffeite or truscottite remain unknown. It is possible to estimate these properties by using different methods such as the polyhedral decomposition method developed by Robinson and Haas (1983), Chermak and Rimstidt (1989) and La Iglesia and Felix (1994). Compared to Helgeson et al. (1978) models, they may be extended to all thermodynamic properties of minerals, as has been shown by La Iglesia and Felix (1994) and they rely on a larger set of calibration minerals. Following La Iglesia and Felix (1994), we have developed a polyhedral decomposition model in order to calculate the $\Delta G^0_{f,298}$, $\Delta H^0_{f,298}$, Cp°_{298} and V^0 of C-S-H. We have considered the $Cp^\circ(T)$ function constant with temperature for sake of precision and simplicity. In our case, this aspect nevertheless has a limited interest because we have used Cp°_{298} estimates by Babushkin et al. (1985) in the previous refinement process.

2.2.3 Verification

The values calculated for $\Delta_f H^0_{Pr,Tr}$ of nanocrystalline C-S-H may be evaluated by comparison with experimental works. Glasser et al. (1998) and (2001) have carried out an important experimental study of cementitious media. They have namely measured the solubility of four nanocrystalline C-S-H (Ca/Si=1.8, 1.4, 1.1 and 0.85), at three different temperatures (25, 55 and 85°C). We have calculated the solubility constants of these phases from solution compositions provided by Glasser et al. (1998) and enthalpies of reaction could be deduced from a 1/T plot and the van't Hoff relation. We have included, the reaction enthalpies derived by Courault (2000), from equilibrium experiments carried out at 25 and 85°C, with two C-S-H (Ca/Si=0.8 and 1.1). A comparison is proposed, in Figure 3, with enthalpies of reaction predicted or refined in this study for nanocrystalline and crystalline C-S-H. For crystalline phases, equilibrium constants are normalised to one Si cation. It may be observed that the estimates for nanocrystalline C-S-H are in agreement with the experimental values.

Finally, it is possible to assess the proposed model by plotting a $CaO\text{-}SiO_2\text{-}H_2O$ phase diagram, as a function of temperature, including phases whose thermodynamic properties have been estimated with this model. This diagram is displayed on Figure 4. It is the same as in Figure 1, except that it includes in addition, truscottite, jaffeite, C2SH and okenite whose properties are estimated with the polyhedral model. We can check the consistency between displayed phase relations among these phases and the other crystalline C-S-H in order to assess the polyhedral model abilities.
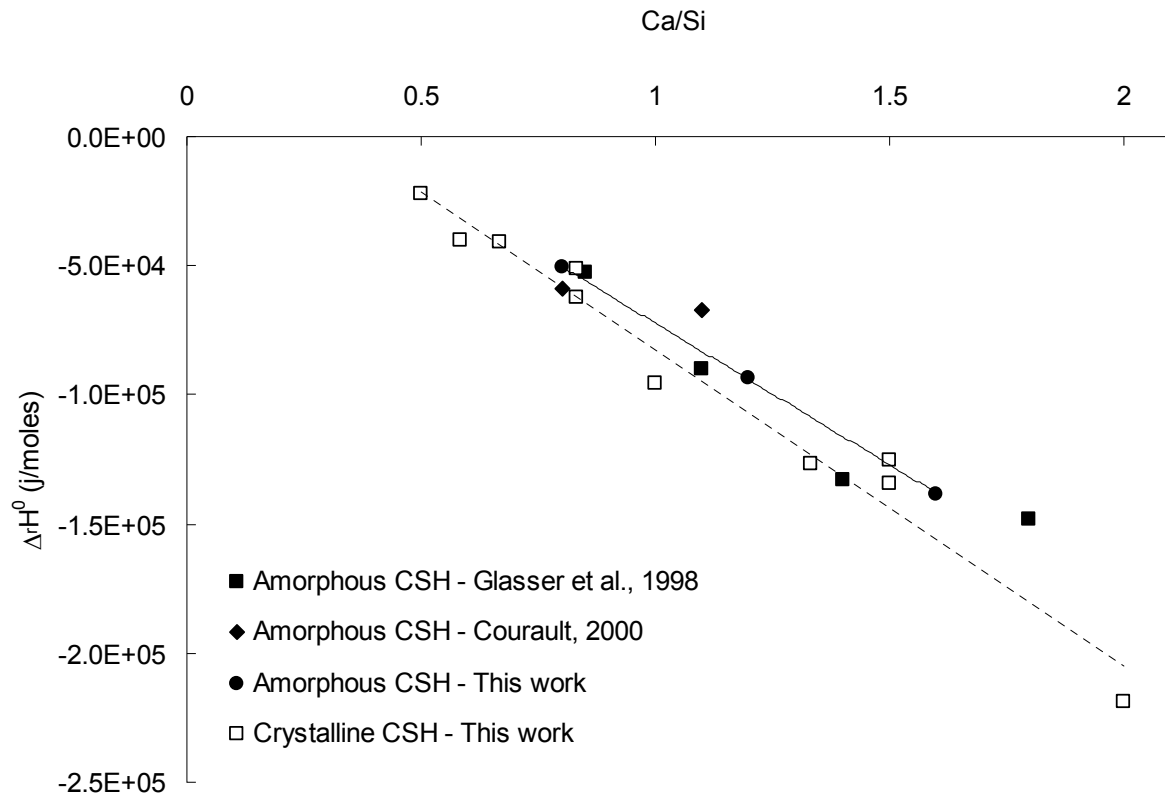
The curves correspond to second order regressions for crystalline C-S-H (dashed line) and first order regressions for nanocrystalline C-S-H (unbroken line, regression on the values estimated in this work). Amorphous CSH stands for nanocrystalline C-S-H.

Figure 3   Equilibrium constant of four nanocrystalline C-S-H, calculated using the solution compositions of Glasser et al. (2001)

The first interesting point in Figure 4 is that nanocrystalline C-S-H1.6, 1.2 or 0.8 do not display a stability domain even if temperature may influence their solubility (Lothenbach et al., 2008). This is consistent with the preceding observations concerning phase relations between nanocrystalline and crystalline polymorphs. In addition, the phase diagram is found to be consistent with literature data (Blanc et al., 2010a) even for okenite, truscottite or C2SH, for which thermodynamic properties are entirely estimated with the polyhedral model.
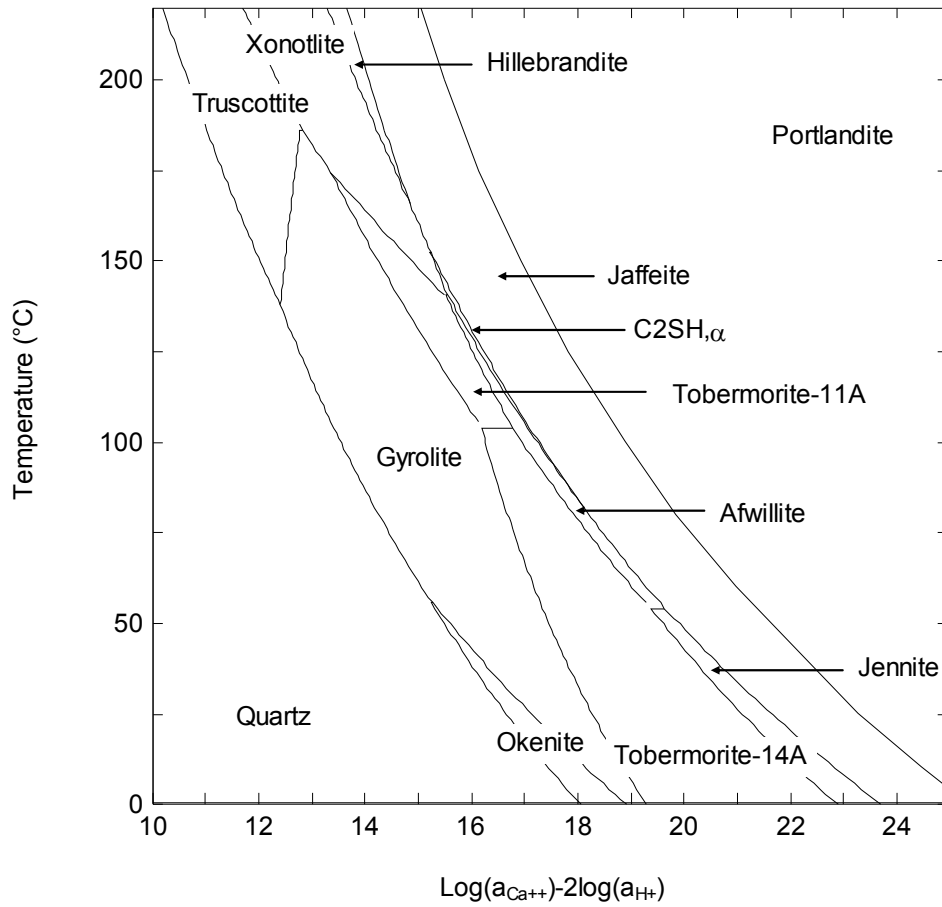
Figure 4   *Phase diagram in the CaO-SiO₂-H₂O system, adding phases of estimated properties*

3 DEVELOPMENT OF THE CEMENTITIOUS MODEL: CEMENT PHASES OTHER THAN C-S-H

Instead of providing an extensive discussion for each of the phases, there follows a full discussion concerning ettringite, as an example showing the way we have proceeded this selection. Thereafter, the properties gathered for the other phases will be reported into a single table, with specific comments when required.

For mineral phases other than C-S-H, we have tried not to create new data but instead to select the solubility study that could best match the selection guidelines. On the other hand, the composition of nanocrystalline C-S-H single phase or end-members is still a matter of discussion. In the present work those compositions were indeed extracted from experimental datasets, together with the corresponding equilibrium constants. This case is different from the other phases, which case is illustrated by the ettringite example.

The phases belonging to this system (ettringite, monosulfoaluminate, C4AH13 and C3AH6) have been much studied namely because the precipitation of secondary ettringite ($Ca_6A_{l2}(SO_4)_3(OH)_{12}$:$26H_2O$) can be responsible for swelling in concrete, leading to fractures and finally to a loss in compressive strength.

3.1 EXAMPLE: THE CASE OF ETTRINGITE $CA_6AL_2(SO_4)_3(OH)_{12}$:$26H_2O$

The selection presented here is first based on calorimetric measurements available in the literature. We have also taken into account the results obtained by equilibrating minerals phases with aqueous solutions. In that case, we have tried to retain only the aqueous solution composition which has an ionic charge balance discrepancy less than 5%. Indeed, in some cases, the discrepancy is higher. According to Myeni et al. (1998), this problem can arise from different problems in the experiments i.e.: (1) kinetic factors that delay the establishment of equilibrium, (2) the compositions of the synthetic phases, which can deviate from theoretical compositions or even include the presence of impurities (3) carbonation of the system. This latter point corresponds to a particular case of "pollution" of the theoretical chemical system by foreign elements. This situation is not surprising in cementitious systems in so far as aqueous solutions are systematically alkaline and strongly basic. The other main criteria retained for this selection are the duration and the reversibility of the experiments considered. The three criteria, electroneutrality, duration and reversibility constitute our main selection criteria.

3.1.1 Previous works on ettringite solubility

To date, a lot of papers had been published about the solubility of ettringite. The experimental studies finally retained in accordance with the selection criteria are listed in Table 2. The constants are calculated after the following reaction:

$$Ca_6Al_2(SO_4)_3(OH)_{12}:26H_2O + 12H^+ = 6Ca^{++} + 2Al^{+++} + 3SO_4^{--} + 38H_2O$$
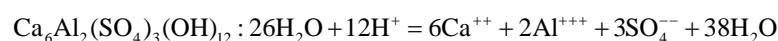
This table also shows the values of the equilibrium constants obtained by adjusting the pH value for sake of electroneutrality. The difference with the values calculated from raw aqueous compositions gives an indication about the quality of both the experimental process and the analyses performed.

Based on Table 2, we have selected the experimental constant calculated by means of Warren and Reardon (1994) experimental results, i.e. LogK = 56.97 ± 0.50. In that case, LogK values obtained by adjusting or not pH are identical. Furthermore, equilibrium is reached both from under-saturation and from over-saturation.

3.1.2 Calorimetric data

Globally, few calorimetric measurements have been acquired to date, for cement phases. For ettringite, we could collect only the $Cp°(T)$ function determined experimentally by Ederova and Satava (1979). In addition, Berman and Newman (1963) have measured $\Delta H°_{f,298}$ directly, from room temperature, acid dissolution calorimetry. In the original paper, the value is obtained from a thermodynamical cycle implying the hydrogarnet phase, C3AH6. Since the selected $\Delta H°_{f,298}$ comes from more recent work from Schoenitz and Navrotsky (1999), its value is slightly different thank that used by Berman and Newman (1963), -5551.50, instead of -5548.00 kJ/mol. We have taken this modification into account in the thermodynamical cycle used by Berman and Newman (1963), leading to -17544.53, instead of -17547.70 kJ/mol, originally. The $Cp°(T)$ function and the corrected $\Delta H°_{f,298}$ value are the only thermodynamic properties measured by calorimetry.

3.1.3 The LogK(T) function calculation and comparison with solubility data extracted from previous works

In the following, we are considering the thermodynamic function selected previously and we are comparing the Log K(T) function calculated with respect to the solubility measured by various authors, as a function of temperature. It must be understand that no fitting process is implied here. The selected thermodynamic functions are:

- Log K_{298} from Warren and Reardon (1994), = 56.97

- $Cp°(T)$ function from Ederova and Satava (1979)

- $\Delta H°_{f,298}$ from Berman and Newman (1963), corrected for the formation enthalpy of C3AH6.

It has to be said that Ederova and Satava (1979) and Berman and Brown (1963) have directly measured, by calorimetry, the Cp(T) and $\Delta H^0_{f,298}$ of ettringite. This type of experiment is well suited for such measurement, namely because it is independent from aqueous equilibria. In Figure 5 is displayed a comparison between the Log K(T) function, calculated with selected thermodynamic constants and solubility data gathered throughout the literature. The more recent results from MacPhee and Barnett (2004) are not displayed there since the authors do not report measured values for pH. For sake of simplicity, at 25°C, only le mean equilibrium constants are reported. No fitting procedure is implied here. It appears that the agreement with literature data is rather close. It is especially close to Perkins and Palmer (1999) results, which are considered by Matschei et al. (2007) as among the more accurate experiment series performed to date. Indeed, equilibrium is reached from both under and supersaturation and most of the solution composition display an electroneutrality discrepancy less than 5%. In addition, the agreement between calculated and experimental values allows to check the Consistency between Warren and Reardon (1994), Berman and Newman (1963) and Ederova and Satava (1979) measurements.

Table 2   *Selection of exp. data related to the solubility of ettringite at 25°C*

References	Method	Reaction time (days)	Number of solutions retained	Log K$_{298}$	Standard deviation
Perkins and Palmer (1999)	Dissolution and precipitation	14 – 22	4	57.29 (*)	0.16
				56.96 (**)	0.28
Ghorab et al. (1998b)	Dissolution only	14	1	60.28 (*) (30°C)	
Glasser et al. (1998)	Dissolution only	151	1	56.88 (*)	
				57.68 (**)	
Atkins et al. (1992)	Dissolution only	14	3	57.08 (*)	0.70
Warren and Reardon (1994)	Dissolution and precipitation		9	56.97 (*)	0.50
				56.97 (**)	0.48
Damidot et al. (1994)	Dissolution only	56	8	56.79 (*)	0.22
Myeni et al. (1998)	Dissolution and precipitation	19	2	57.30 (*)	0.34
		21		56.60 (**)	0.11

(*) Log K$_{298}$ calculated from experimental solutions, by adjusting pH for sake of electroneutrality ; (**) without adjusting pH.
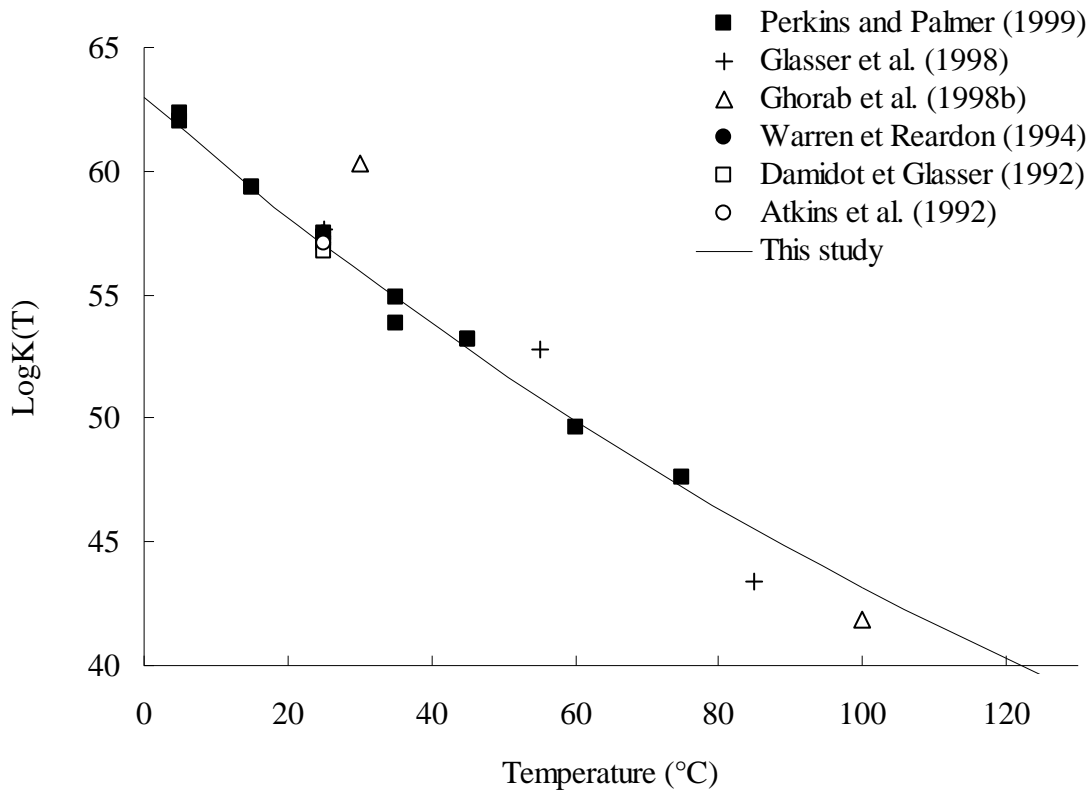
Legend:
- ■ Perkins and Palmer (1999)
- \+ Glasser et al. (1998)
- △ Ghorab et al. (1998b)
- ● Warren et Reardon (1994)
- □ Damidot et Glasser (1992)
- ○ Atkins et al. (1992)
- — This study

Figure 5   *Solubility of ettringite as a function of temperature*

3.1.4 Phase relation through the drawing of predominance diagrams

The selection of thermodynamic constants allows us to realize predominance diagrams in different chemical systems, as a function of temperature. Such diagrams are first drawn in order to verify the predicted phase relations. They may also be of help when no other data are available. Finally, they help in understanding the temperature and composition effects on mineral stability ranges.

Predominance diagrams for the system $CaO\text{-}Al_2O_3\text{-}SO_3\text{-}H_2O$, including the temperature dependency, are represented in Figure 6 and Figure 7. Figure 6 shows that, in the presence of portlandite and C3AH6, monosulfoaluminate is stable between 65 and 121°C. It is then transformed into ettringite + C3AH6 when T < 65°C and into anhydrite + C3AH6 when T > 121°C. For aluminate phases, the diagram presented in Figure 7 shows that the transition temperature between C4AH13 and C3AH6 varies as a function of the $Al^{+++}/(H^+)^3$, the highest temperature being reached when the solution becomes saturated with respect to portlandite. Both series of observations are consistent with the evolution of phase relations with temperature as described by Taylor (1992) or Ghorab et al. (1998a and b).
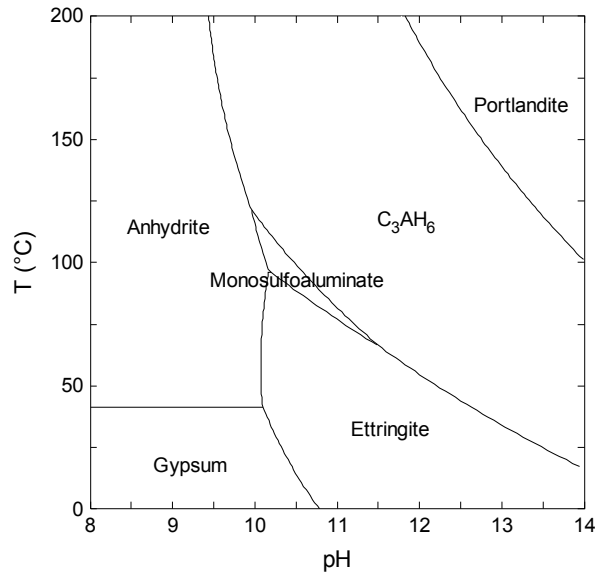
Figure 6   *Phase relations in the system CaO-Al$_2$O$_3$-SO$_3$-H$_2$O, as a function of temperature. The solution is saturated with respect to gibbsite and [SO$_4^-$]$_T$ = 1 mmol/l*
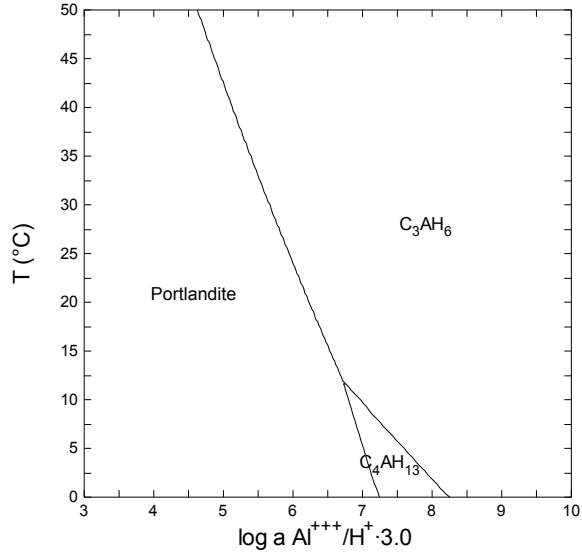
Figure 7   *Phase relations in the system CaO-Al$_2$O$_3$-H$_2$O as a function of temperature, [Ca^{2+}] = 10^{-2}*

3.2 OTHER CEMENT PHASES

The thermodynamic constants finally selected here are given in Table 3, together with the equilibration reactions considered. The selection from literature data operates as described for ettringite:

- A Log K_{298} is first retained, according to the criteria explained above
- It is completed with $\Delta H°_{f,298}$ and $Cp°(T)$ functions measured by calorimetry. When either or both are not available, we use Helgeson et al. (1978) model in order to estimate $S°298$ and $Cp°_{298}$
- The Log K(T) function is calculated from the thermodynamic function previously selected. Then, it is compared with solubility data found in previous experiments.

In our case, the comparison with solution equilibria experiment represents a first verification for selected constants.

The selection results are summarized into Table 3. For each phase, the whole selection process is described into Blanc et al. (2010b). Thus the entire process is not fully described into the present document. We just propose here, in addition to Table 3, some specific comments:

Katoite

For Si substituted hydrogarnets, the selection of Log K_{298} is quite unsatisfactory because of a lack of reliable experimental data

Monosulfoaluminate

Some uncertainties in literature seem to arise from the fact that the phase may possibly not be stable at room temperature. This problem is found both for solution experiments and the calorimetric measurements, after long reaction times or after the synthesis process. More details are given in Blanc et al. (2010b)

Hydrotalcite

The lack of data at different temperatures forbids to verify the reliability of the calculated LogK(T) function

Fe-bearing phases

$LogK_{298}$ are based only on Moschner et al. (2008) work. The LogK(T) functions could not be verified because of a lack of experimental data.

Table 3 *Thermodynamic properties of cementitious phases, selected or estimated in this work*

Name	Reaction	LogK (1)	LogK (2)	$\Delta_f G^0_{Pr,Tr}$ kJ.mol^{-1}	$\Delta_f H^0_{Pr,Tr}$ kJ.mol^{-1}	$S^0_{Pr,Tr}$ kJ.mol^{-1}	Cp 25°C J.mol^{-1}.K^{-1}	V cm³.mol^{-1}
	CaO-Al$_2$O$_3$-SiO$_2$-H$_2$O system							
Grossular	$Ca_3Al_2Si_3O_{12} + 12H^+ = 2Al^{+++} + 3Ca^{++} + 3H_4SiO_4$		*49.35*	*-6279.46*	*-6640.00* [a]	*260.10* [a]	*326.50* [a]	*125.28* [a]
Katoite	$Ca_3Al_2(SiO_4)(OH)_8 + 12H^+ = 2Al^{+++} + 3Ca^{++} + 8H_2O + H_4SiO_4$	68.49 (0.8Si)	71.16 [c]	*-5433.82*	*-5907.82*	*364.00* [E]	*415.07* [E]	*141.51* [E]
Straetlingite	$Ca_2Al_2SiO_2(OH)_{10}:2.5H_2O + 10H^+ = 2Al^{+++} + 2Ca^{++} + 10.5H_2O + H_4SiO_4$	49.82	49.66 [c]	*-5596.58*	*-6216.78*	*545.88* [E]	*521.48* [E]	*215.63* [b]
	CaO-Al$_2$O$_3$-SO$_3$-CO$_2$-Cl-H$_2$O system							
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}:26H_2O + 12H^+ = 2Al^{+++} + 6Ca^{++} + 38H_2O + 3SO_4^{--}$	56.80	56.97 [d]	*-15210.23*	*-17544.53* [f]	*1883.59*	*2174.36* [g]	*710.32* [i]
Monosulfoaluminate	$Ca_4Al_2(SO_4)(OH)_{12}:6H_2O + 12H^+ = 2Al^{+++} + 4Ca^{++} + 18H_2O + SO_4^{--}$	72.44	73.07 [c]	*-7781.90*	*-8763.68* [c]	*786.94*	*942.42* [g]	*311.26* [i]
Hydrogrossular	$Ca_3Al_2(OH)_{12} + 12H^+ = 2Al^{+++} + 3Ca^{++} + 12H_2O$	80.86	80.32 [c]	*-5020.87*	*-5551.50* [h]	*416.61*	*459.35* [g]	*149.52* [a]
C4AH13	$Ca_4Al_2(OH)_{14}:6H_2O + 14H^+ = 2Al^{+++} + 4Ca^{++} + 20H_2O$	104.30	103.65 [c]	*-7337.63*	*-8318.00* [k]	*685.13*	*798.90* [E]	*269.20* [j]
Monocarboaluminate	$3CaO.Al_2O_3.CaCO_3:10.68H_2O + 13H^+ = 2Al^{+++} + HCO_3^- + 4Ca^{++} + 16.68H_2O$	80.56	80.55 [c]	*-7269.02*	*-8175.75* [f]	*601.89*	*730.82* [E]	*261.96* [j]
Hemicarboaluminate	$6CaO.2Al_2O_3.CaCO_3.Ca(OH)_2:21H_2O + 27H^+ = 4Al^{+++} + HCO_3^- + 8Ca^{++} + 37H_2O$	183.47	183.66 [c]	*-14685.62*	*-16600.31*	*1269.09* [E]	*1531.53* [E]	*569.02* [j]
Friedel's salt	$2Ca_2Al(OH)_6Cl:2H_2O + 12H^+ = 2Al^{+++} + 4Ca^{++} + 2Cl^- + 16H_2O$		74.93 [c]	*-6815.44*	*-7670.04* [k]	*527.70*	*692.86* [E]	*276.24* [j]
	Mg bearing phases							

Name	Reaction	LogK (1)	LogK (2)	$\Delta_f G^0_{Pr,Tr}$ kJ.mol^{-1}	$\Delta_f H^0_{Pr,Tr}$ kJ.mol^{-1}	$S^0_{Pr,Tr}$ kJ.mol^{-1}	Cp 25°C J.mol^{-1}.K^{-1}	V cm³.mol^{-1}
CaO-Al$_2$O$_3$-SiO$_2$-H$_2$O system							
Hydrotalcite	$Mg_4Al_2(OH)_{14}:3H_2O + 14H^+ = 2Al^{+++} + 4Mg^{++} + 17H_2O$	73.68	73.74 [c]	-6407.21	-7219.64	512.96 [E]	556.15 [E]	227.36 [j]
CO3-hydrotalcite	$Mg_4Al_2(OH)_{12}(CO_3):2H_2O + 13H^+ = 2Al^{+++} + HCO_3^- + 4Mg^{++} + 14H_2O$		61.19 [n]	-6295.37	-7078.83	552.07	604.15 [E]	231.46 [j]
Brucite	$Mg(OH)_2 + 2H^+ = Mg^{++} + 2H_2O$	16.84	17.10 [m]	-832.05	-924.50 [m]	58.42	77.27 [t]	24.63 [a]
Fe bearing phases							
C4FH13	$Ca_4Fe_2(OH)_{14}:6H_2O + 14H^+ = 2Fe^{+++} + 4Ca^{++} + 20H_2O$	93.96	95.12 [c]	-6443.63	-7417.40 [E]	705.35 [E]	787.08 [E]	274.40 [j]
C3FH6	$Ca_3Fe_2(OH)_{12} + 12H^+ = 2Al^{+++} + 3Ca^{++} + 12H_2O$	70.63	72.37 [c]	-4123.57	-4647.59 [E]	436.84 [E]	484.15 [E]	154.50 [j]
Fe-ettringite	$Ca_6Fe_2(SO_4)_3(OH_{)12}:26H_2O + 12H^+ = 2Fe^{+++} + 6Ca^{++} + 38H_2O + 3SO_4^{--}$	54.57	54.55 [c]	-14281.38	-16601.22	1930.11 [E]	2214.54 [E]	711.80 [j]
Fe-monosulphate	$Ca_4Fe_2(SO_4)(OH)_{12}:6H_2O + 12H^+ = 2Fe^{+++} + 4Ca^{++} + 18H_2O + SO_4^{--}$	65.97	66.05 [c]	-6879.31	-7846.68	833.30 [E]	982.61 [E]	316.06 [j]

[c] calculated from experiments, this work; [E] estimated using Helgeson et al. (1978) model; [a] Robie and Hemingway (1995); [b] According to the density obtained by Rinaldi et al. (1990); [d] Warren and Reardon (1994); [f] Berman and Newman (1963); [g] Ederova and Satava (1979); [h] Schoenitz and Navrotsky (1999); [i] Moore and Taylor (1970); [j] According to the density provided by Taylor (1992); [k] Houtepen and Stein (1976); [m] Altmaier et al. (2003), selection discussed by Blanc et al. (2006), [n] Johnson and Glasser (2003). The values in italics have been recalculated using the values in normal characters.

(1) Matschei et al. (2007), except for Brucite (Lothenbach et al., 2008)

(2) This selection

4 COMPARISON WITH PREVIOUS SELECTION

Lothenbach et al. (2008) have published a full solubility model for all cement phases, based on the experiments of Matschei et al. (2007) and Moschner et al. (2008) and on a literature review. In Table 3, we provide a comparison with the Log K_{298} extracted by Lothenbach et al. (2008) from the experiments.

The main differences with those authors arise from the following phases: C3AH6, katoite, monosulfoaluminate, C4AH13 and Fe-ettringite. Here follows a short discussion concerning the discrepancies between two groups of equilibrium constants:

- C3AH6 : the constant provided by Matschei et al. (2007) is the highest found among 5 different group of authors. The Log K_{298} value retained by Lothenbach et al. (2008), 80.86, is found by considering the experiments performed from under saturation only. In the present study, we have preferred a constant extracted from Glasser et al. (1998), 80.32, based on dissolution experiments which have lasted 173 days, against 84 for Matschei et al. (2007).

- Katoite : It had been shown by Blanc et al. (2010b) that the value found by Matschei et al. (2007) may have undergo an incomplete dissolution leading to small value of the equilibrium constant

- monosulfoaluminate : Matschei et al. (2007) experiments lead the authors to consider the stability of monosulfoaluminate at 25°C

- C4AH13: the LogK we have selected is based on an invariant point whose temperature is just inferred from phase relations. On the other hand, Matschei et al. (2007), after 430 days of reaction time, observe that C4AH13 disappear almost completely. C3AH6 forms instead, which could explain part of the discrepancy with our selection.

Recently, Damidot et al. (2011) have compared the Cem07 database (Lothenbach et al., 2008) with the present work. They first have concluded that differences in equilibrium constants lie within the uncertainty range. The stability of monosulfoaluminate extracted by Blanc et al. (2010b) is partially based on a temperature limit of 65°C. In addition, we can notice that, in a previous work, Damidot and Glasser (1992) predicted a rather similar temperature of 50°C for the appearance of monosulfoaluminate. Finally, it appears that this point cannot be clarified based only on LogK(T) functions because of their uncertainty ranges. It would require additional experiment devoted to the equilibrium temperature of assemblage C3AH6/ettringite/monosulfoaluminate.

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