TCIII- 2022- 01E



ThermoChimie Technical report

Cement Minerals Documentation



20 Janaury 2022

The ThermoChimie database was first developed in 1995 by Andra, the French national radioactive waste management agency. They have since been joined by Radioactive Waste Management (RWM) from the UK, and ONDRAF/NIRAS from Belgium.

ThermoChimie provides an accurate and consistent set of data specifically chosen for use in modelling the behaviour of radionuclides in waste packages, engineered barriers, and both the near surface and deep geosphere. The database can be used to model the speciation and solubility of a wide range of stable and radioactive elements, organics, and solid phases including cements, clay minerals and degradation products (such as zeolites). The database is suitable for use within the range of conditions expected in both near-surface and geological disposal facilities: pH 6-14, ionic strength up to SIT, Eh within the stability fields of water, and temperatures from 15 to 80°C.

ThermoChimie is intended for use across the radioactive waste management community, to support repository performance assessment, research and development activities and decision making. To maximise their utility the data are therefore provided in formats suitable for use with common geochemical modelling codes. The database can be viewed and downloaded from the project website: <u>https://www.thermochimie-tdb.com/</u>, where additional information and supporting documents are also available.

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 presenting the solubility constants of the minerals that compose cement pastes, based on the selection published by Blanc et al. (2010a) and Blanc et al. (2010b), consistently with the selection of aqueous species realized for the Thermochimie data base (Giffaut et al., 2014). Data selection takes into consideration a range of temperatures from 10 to 100°C. This implies to focus the selection not only on the equilibrium constants at 25°C but also on the enthalpy of formation and the heat capacity of each mineral. The chemical system investigated is a complex one, CaO-SiO2-Al2O3-MgO-Fe2O3-CO2-SO3-CI-H2O. The selection includes crystalline and nanocrystalline gel-phases C-S-H phases (CaO-SiO2-H2O system, Blanc et al. (2010a)) and accessory minerals such as AFm (alumina, ferric oxide, monosulfate) Aft (alumina, ferric oxide, trisulfate) phases, for example, from the CaO-Al2O3-MgO-Fe2O3-CO2-SO3-CI-H2O system (Blanc et al., 2010b).





ANDRA Radioactive Waste Management

1. Selection guidelines

The selection for thermodynamic properties of cementitious minerals is carried out according to the following guidelines :

- to avoid fitting LogK(T) functions, as well as averaging equilibrium constants. The aim is to avoid producing some new and perhaps confusing data ;
- when available, to favor calorimetric measurements and to compare the resulting LogK(T) functions with experimental solubilities in order to get an assessment involving different experimental technics;
- to select solution equilibria experiments based on the assessment of the electroneutrality balance, the duration of the experiment and the experimental protocol used by the authors ;
- to extract equilibrium constants from solution equilibria using the Thermochimie database aqueous species ;
- to verify systematically the selection 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 AI^{+++} , Ca^{++} , H_4SiO_4 , Ca^{++} , Mg^{++} , Fe^{+++} , CO_3^{--} , CI^- , 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 the GWB software (Bethke, 2004). The activity coefficient model used is extended Debye-Hückel (Helgeson, 1969).

In addition, we have adopted a convention for chemical notation specific to the cementitious materials (Taylor, 1997), to designate chemical compositions of minerals:

C = CaO; S = SiO₂; A = Al₂O₃, M = MgO, F = Fe₂O₃ and H = H₂O.

2. The CaO-SiO2-H2O system

C-S-H are the mineral phases that provide to the cement the main part of its hydraulic binder properties. They are formed by hydration of the C3S and C2S phases or during pozzolanic reactions. Crystalline C-S-H appear with high temperatures, enhancing crystallization (Atkins et al., 1994). At lower, room temperature, the polymerization of tetrahedral SiO₂ is less efficient and C-S-H with a poorer polymerization precipitate, initially as dimers then pentamers (Chen et al., 2004; Thomas et al., 2003), and silicate chain with higher lengths as polymerization goes on.

2.1. CRYSTALLINE PHASES

From Richardson (2008) review, the crystalline C-S-H belong to various mineralogical groups like the tobermorite, jennite or gyrolite groups. The interest lies in the possible transition between amorphous to crystalline C-S-H, especially with increasing the temperature and/or the reaction time, which could induce modifications, especially in the Ca and Si dissolved concentrations.

2.1.1. Field observations

Field observations can be of use in order to precise phase relations among crystalline C-S-H phases. In that case, the equilibration time may correspond to hundreds of thousands of years while, in most cases, equilibration experiments may last for weeks or months, at best. It may consequently be assumed that the minerals observed in natural contexts have reached the most stable thermodynamic equilibrium state.

This would be the case for jennite $(Ca_9Si_6O_{16}(OH)_{10}:6(H_2O))$ and tobermorite (Ca₅Si₆O_{16.5}(OH):5H₂O) (Smellie, 2000), observed as fracture infilling on several samples from the Magarin site (Jordan). This would also be the case for jennite and afwillite (Ca₃Si₂O₄(OH)₆), 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 (Ca₂Si₃O_{7.5}(OH):2H₂O) and okenite (CaSi₂O_{5:}2H₂O) are usually found associated with low temperature zeolites like apophyllite (Sukheswala et al., 1974), itself related to chabazite (Keith and Staples, 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 $(Ca_6Si_6O_{17}(OH)_2)$ 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 (Ca₇Si₁₂O₂₉(OH)₄.H₂O) related to laumontite, which requires a higher formation temperature between 180 and 300°C (Rancon, 1985). Concernina Hillebrandite $(Ca_2SiO_3(OH)_2:0.17H_2O)$ and foshaqite (Ca₄Si₃O₉(OH)₂:0.5H₂O), these minerals have been observed in natural samples of the Bushveld skarn formation by Buick et al. (2000). Jaffeite (Ca₆(Si₂O₇)(OH)₆) 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, iennite, xonotlite, foshagite, tobermorite, gyrolite and okenite. Among these, afwillite, iennite, gyrolite and okenite should be restricted to low temperature domains.

2.1.2. Available thermodynamic data

Among the few calorimetric data available for crystalline 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 11Å, 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) estimates. On the other hand, with respect to the measurements carried out by Zuern and Fehr (2000), the discrepancy was 3.5 kJ/mol only. We have selected the value provided by Zuern and Fehr (2000).

2.1.3. Refinement of the phase diagram for crystalline C-S-H

Phase transitions have been refined by using constraints issued from a bibliographic review that provides transition temperatures for several mineral assemblages (Blanc et al., 2010a). In addition, we have calculated a linear relation between Babushkin et al. (1985) estimates for $S^{\circ}_{Pr,Tr}$ and Cp(298 K): Cp(298 K) = 1.15 * $S^{\circ}_{Pr,Tr}$ - 28.39, where R^{2} = 0.993. Finally, we have completed the thermodynamic datasets with the enthalpies of formation previously selected for tobermorite-11Å, hillebrandite, xonotlite and foshagite.

The thermodynamic properties calculated for crystalline C-S-H are given in Table 1, and the resulting phase relations are displayed on Figure 1. The latter indicates that the stable phases at 25°C are jennite, tobermorite-14Å, hillebrandite and gyrolite. As temperature increases, gyrolite and hillebrandite remain stable and afwillite, tobermorite-11Å then xonotlite appear successively. It is interesting to verify that jennite can actually be among the thermodynamically stable phases in the low temperature part of 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 stable minerals. It is possible that 170°C for the afwillite-hillebrandite-foshagite assemblage is a somewhat low temperature; Speakman (1968), for example, have synthetized foshagite only for temperatures higher then 259°C. A part from this case, the refinement comes to a close agreement with constraints extracted from the literature (Blanc et al., 2010a).



Figure 1 - Phase diagram in the CaO-SiO₂-H₂O system, thermodynamic properties refined in this work

				/					
Name	Formula	Log K(298)		∆G ⁰ _{f,298} kJ/mol	∆□H ⁰ _{f,298} kJ/mol	S ⁰ _{f,298} J/mol.K	Cp° ₂₉₈ J/mol.K	V° cm ³ /mol	
Crystalline C-S-H									
gyrolite	Ca ₂ Si ₃ O _{7.5} (OH):2H ₂ O	22.34 ^b		-4550.06	-4917.99 ^b	309.32	325.94 ^b	137.34 ^e	
xonotlite	Ca ₆ Si ₆ O ₁₇ (OH) ₂	91.34 ^b		-9465.12	-10022.15 ^b	573.74	628.64 ^b	256.90°	
tobermorite-14A	Ca ₅ Si ₆ O _{16.5} (OH):10H ₂ O	62.9	4 ^b	-11090.12	-12175.15 ^b	874.57	973.53 ^b	351.30°	
tobermorite-11A	Ca₅Si ₆ O _{16.5} (OH):5H ₂ O	65.58 ^b		-9889.25	-10680.92 ^b	692.55	764.91 ^b	286.19 ^e	
foshagite	Ca ₄ Si ₃ O ₉ (OH) ₂ :0.5H ₂ O	65.96 ^b		-5643.83	-6032.43 ^b	295.07	309.38 ^b	160.66 ^e	
jennite	Ca ₉ Si ₆ O ₁₆ (OH) ₁₀ :6(H ₂ O)	147.3	3 ^b	-13886.77	-15189.04 ^b	839.25	933.21 ^b	456.40 ^e	
afwillite	Ca ₃ Si ₂ O ₄ (OH) ₆	49.42 ^b		-4469.06	-4853.82 ^b	289.70	303.55 ^b	129.53 ^e	
hillebrandite	Ca ₂ SiO ₃ (OH) ₂ :0.17H ₂ O	36.95 ^b		-2481.95	-2662.48 ^b	179.71	177.46 ^b	72.58 ^e	
truscottite	Ca ₇ Si ₁₂ O ₂₉ (OH) ₄ .H ₂ O	77.08		-15280.40 ^d	-16854.62 ^d	927.68	1034.10 ^d	478.73 ^e	
okenite	CaSi ₂ O _{5:} 2H ₂ O	9.18		-2881.72 ^d	-3135.70 ^d	208.52	210.07 ^d	94.77 ^e	
C₂SH,□	Ca ₂ (HSiO ₄)(OH)	35.54		-2449.12 ^d	-2634.92 ^d	122.38	111.88 ^d	71.12 ^e	
jaffeite	Ca ₆ (Si ₂ O ₇)(OH) ₆	114.06		-6469.94 ^d	-6972.77 ^d	326.19	344.90 ^d	174.38°	
Nanocrystalline C-S-H									
C-S-H1.6	Ca _{1.6} SiO _{3.6} :2.58H ₂ O	29.27ª (1.67 Ca)	28.00 ^c	-2550.86	-2819.79 ^d	154.42	190.10 ^d	84.68 ^e	
C-S-H1.2	Ca _{1.2} SiO _{3.2} :2.06H ₂ O		19.30°	-2161.23	-2384.34 ^d	129.14	162.13 ^d	71.95°	
C-S-H0.8	Ca _{0.8} SiO _{2.8} :1.54H ₂ O	11.20ª (0.83 Ca)	11.05 [°]	-1769.03	-1945.13 _d	107.85	138.38 ^d	59.29 ^e	

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

(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 LogK₂₉₈ and its $\Delta H^0_{r,298}$).

2.2. NANOCRYSTALLINE C-S-H PHASES

Nanocrystalline C-S-H (CaO-SiO₂-H₂O) hydrates represent about or more than 50% in weight of a cement paste, hydrated at ambient temperature. C-S-H is responsible for most of the hydraulic binding capacity of the material. It is formed after hydration of C₃S and C₂S primary phases or during pozzolanic reactions with free lime (Taylor, 1997). Macroscopically, it consists in a gel-like material, infilling the pore structure of the cement paste. The particles are sub-micron sized and their morphology may depend on the space available in the pore structure and on the initial composition of the paste (Richardson, 1999). C-S-H degree of polymerization depends on the chemical media, ageing time and temperature (Taylor, 1997). Structural models have been developed in order to account, in the structural formula, for the degree of polymerization, the degree of hydration and the composition variation.

Calcium silicate hydrates are composed by SiO_4^4 tetrahedra, organized in polymerized chains, which are connected by a layer built up by sevenfold coordinated calcium cations (Merlino et al., 2001) and Ca²⁺ cations and H₂O molecules in interlayer sites (Cong and Kirkpatrick, 1996). The structure is closely related to that of tobermorite 14Å (Richardson, 2014), although undergoing structural defects, e.g. variable degree of polymerization for the silicate chains.

2.2.1. Solubility

Since the early attempts by Glasser et al. (1987), Berner (1988), Atkinson et al. (1989), various models have been proposed to describe C-S-H solubility. Some of them have been the subject of extended reviews by (Benbow et al., 2007; Clodic and Meike, 1997; Soler, 2007). Among the models, some authors have considered a continuous variation of the equilibrium constant while composition is modified (Berner, 1988). This is especially the case for solid solution models (Kulik, 2011; Myers et al., 2015; Walker et al., 2007), including the recent development by Walker et al. (2016). Other models prefer to rely on fixed compositions (Blanc et al., 2010a; Nonat, 2004; Stronach and Glasser, 1997) especially since those are easy to integrate into geochemical codes. The drawback is that it will display a scaled evolution of the total dissolved Ca or Si (Blanc et al., 2010a) vs solid composition.

In order to estimate the composition and the solubility of three C-S-H phases, we have collected a experimental datasets providing the composition of the solution equilibrated with C-S-H. The collected data are displayed in Figure 2. From these data, Blanc et al. (2010a) have calculated the Ca/Si ratio for three different C-S-H phases: $C/S = 1.6 \pm 0.10$; 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). Then, solubilities are fitted through a least-squared process for the 4 phases (3 C-S-H and portlandite), leading to the following LogK(298 K) values:

- C-S-H1.6: LogK(298 K) = 28.00
- C-S-H1.2: LogK(298 K) = 19.30
- C-S-H0.8: LogK(298 K) = 11.05
- Portlandite : LogK(298 K) = 22.81

The latter value is identical to the 22.81±0.4 value provided by Reardon (1990) and Glasser et al. (2001). It is also close to the value of 22.80 found by Hummel et al. (2002) and Nordstrom et al. (1990). Figure 2 compares the results obtained with respect to experimental data. In addition, we could calculate that an ideal solid solution based on C-S-H0.8 and 1.6 end members would provide an interesting alternative, avoiding the scaled pattern due to the fixed compositions.



Figure 2 - Relation between C/S in C-S-H and dissolved calcium concentration, according to different authors

2.2.2. Polyhedral model

Direct measurements are lacking in the literature for the enthalpy of formation and the heat capacities of nanocrystalline C-S-H. Values determined by (Roosz et al., 2018) can not be used directly because their compositions are different from the compositions determined by Blanc et al. (2010a). 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 Félix (1994). This approach can be applied to each thermodynamic property of the minerals, as shown by La Iglesia and Felix (1994). 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 V⁰ of C-S-H. We have considered a constant $Cp^{\circ}(T)$ function with temperature, for sake of precision and simplicity. More details on this development are given in Blanc et al. (2010a).

2.2.3. Verification

The values estimated for $\Delta_f H^0_{Pr,Tr}$ of nanocrystalline C-S-H may be evaluated by comparison with experimental works. Glasser et al. (1999) and Glasser et al. (2001) have carried out a large investigation of mineral solubilities in 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

and enthalpies of reaction could then be deduced from a 1/T plot and the Van't Hoff relation. The values are reported on Figure 3, together with 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). The figure allows a positive comparison between these experimental values and the estimates calculated using the polyhedral decomposition model.

Finally, it is possible to assess the proposed model by plotting a CaO-SiO₂-H₂O phase diagram, as a function of temperature, including phases for which the entire set of thermodynamic properties have been estimated with the polyhedral model (truscottite, jaffeite, C2SH and okenite). The diagram is displayed on Figure 4, with similar features than Figure 1, except for the additional phases. Their presence implies new phase relations which have been successfully compared with field observations by Blanc et al. (2010a).

It is interesting to note that in Figure 4, nanocrystalline C-S-H1.6, 1.2 or 0.8 do not display a stability domain; this is consistent with phase relations between nanocrystalline and crystalline polymorphs (Blanc et al., 2010a).



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 4 - Phase diagram in the CaO $-SiO_2-H_2O$ system, adding phases whose thermodynamic properties are estimated in this work (truscottite, jaffeite, C2SH and okenite)

3. Cement phases other than C-S-H

In order to complete the mineral set for cement minerals, it is necessary to define the solubility constants of the mineral phases, other than C-S-H, that constitute cement pastes or which could be produced during the degradation processes. Because the selection is not only focused on solubility at room temperature, it had been extended to the enthalpy of formation and to the heat capacity, for all the minerals of interest.

The present selection is based on the collection published by Blanc et al. (2010b), which is consistent with the aqueous species selected for the Thermochimie database (Giffaut et al., 2014).

3.1.1. Methods and concepts

Globally, the selection follows the guidelines previously reported. In addition, the selection of the cement phases (other than C-S-H) is carried out following two different steps, following a method similar for all of the different mineral types:

- Step 1: Thermodynamic properties are first selected or extracted for each single phase
- Step 2: Phase relations are investigating for different chemical systems through predominance diagrams, in a way to assess the consistency of our selection.

As an illustration, the following sections provide the details of the selection for the mineral ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}$:26H₂O. The properties gathered for the other phases are then reported into a single table, with specific comments when required. Full details for the selection of their thermodynamic properties are given in Blanc et al. (2010b).

3.2. EXAMPLE: THE CASE OF ETTRINGITE CA₆AL₂(SO₄)₃(OH)₁₂:26H₂O

The phases belonging to the sub-system CaO-Al₂O₃-SO₃-H₂O (ettringite, monosulfoaluminate, C4AH13 and C3AH6) have been intensively studied namely because the precipitation of secondary ettringite (Ca₆A_{l2}(SO₄)₃(OH)₁₂:26H₂O) can be responsible for swelling in concrete, leading to fractures, degradation and finally to a loss in compressive strength.

The selection of the thermodynamic properties of ettringite is first based on the calorimetric measurements available in the literature. We have also taken into account the results obtained by equilibrating minerals phases with aqueous solutions. In that regard, we have selected from the literature only the aqueous solution compositions which displayed an ionic charge balance discrepancy < 5%. According to Myneni et al. (1998), higher discrepancies may arise from different issues 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.

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:

$$Ca_{6}Al_{2}(SO_{4})_{3}(OH)_{12}: 26H_{2}O + 12H^{+} = 6Ca^{++} + 2Al^{+++} + 3SO_{4}^{--} + 38H_{2}O$$

Table 2 also shows the values of the equilibrium constants extracted from the experimental works, 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 using 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.

3.2.1. 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 Ederová and Šatava (1979). In addition, Berman and Newman (1963) have measured $\Delta H^{\circ}_{f,298}$ directly, from room temperature, acid dissolution calorimetry. In the original paper, the value is obtained from a thermodynamical cycle implying the hydrogarnet phase, C3AH6. For the latter mineral, $\Delta H^{\circ}_{f,298}$ selected in this work comes from a more recent work from Schoenitz and Navrotsky (1999), its value is slightly different than the value determined 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, for the ettringite enthalpy of formation.

3.2.2. LogK(T) function calculation and comparison with solubility data extracted from previous works

In the following, the Log K(T) function is calculated the thermodynamic function selected previously and the resulting function is compared with respect to the solubility measured by various authors, as a function of temperature. The selected thermodynamic functions are:

- Log K_{298} from Warren and Reardon (1994), = 56.97
- Cp°(T) function from Ederova and Satava (1979)
- $\Delta H^{\circ}_{f,298}$ from Berman and Newman (1963), corrected for the formation enthalpy of C3AH6.

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 results obtained by 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 the mean equilibrium constants are reported, for each authors. No fitting procedure is implied. It appears that the agreement with literature data is rather satisfactory. The matching is especially good with respect to Perkins and Palmer (1999) dataset, which have been considered by Matschei et al. (2007) as very accurate. In Perkins and Palmer (1999) experiments, equilibrium is reached from both under and supersaturation and most of the solution composition display an electroneutrality discrepancy < 5%.

		np: data forato			
References	Method	Reaction time (days)	Number of solutions selected	Log K ₂₉₈	Standard deviation
Perkins and Palmer	Dissolution and	14 – 22	4	57.29 (*)	0.16
(1000)	precipitation			56.96 (**)	0.28
Ghorab et al. (1998b)	Dissolution	14	1	60.28 (*)	
. ,	oniy			(30 C)	
Glasser et al. (1998)	Dissolution	151	1	56.88 (*)	
	Only			57.68 (**)	
Atkins et al. (1992)	Dissolution only	14	3	57.08 (*)	0.70
Warren and Reardon	Dissolution and		9	56.97 (*)	0.50
(1994)	precipitation			56.97 (**)	0.48
Damidot et al. (1994)	Dissolution only	56	8	56.79 (*)	0.22
	Dissolution	19		57.30 (*)	0.34
Myeni et al. (1998)	and		2		
	precipitation	21		56.60 (**)	0.11

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

(*) Log K_{298} calculated from experimental solutions, pH adjusted for sake of electroneutrality; (**) without adjusting pH.



Figure 5 - Solubility of ettringite as a function of temperature

3.2.3. Phase relations investigated through the drawing of predominance diagrams

The selection of thermodynamic constants allows drawing predominance diagrams in different chemical systems, as a function of temperature. Such diagrams are first drawn in order to verify the predicted phase relations and stability domains. They also provide a clear illustration of the temperature and composition effects on mineral stability ranges.

Predominance diagrams for the system CaO-Al₂O₃-SO₃-H₂O, including the temperature dependency, are displayed in Figure 6 and Figure 7. Figure 6 indicates 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 activity ratio, 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 (1997) or (Ghorab et al., 1998a, b).



Figure 6 - Phase relations in the system CaO-Al₂O₃-SO₃-H₂O, as a function of temperature. The solution is saturated with respect to gibbsite and $[SO_4^-]_T = 1 \text{ mmol/l}$



Figure 7 - Phase relations in the system CaO-Al₂O₃-H₂O as a function of temperature, $[Ca^{2^+}] = 10^{-2}$

3.3. OTHER CEMENT PHASES

The thermodynamic constants finally selected for the CaO-Al₂O₃-MgO-Fe₂O₃-CO₂-SO₃-Cl-H₂O chemical system are reported in Table 3, together with the equilibration reactions considered. The selection from literature data operates as described for ettringite:

- LogK₂₉₈ is first selected, according to the criteria explained above
- It is completed with △H°_{f,298} and Cp°(T) functions measured by calorimetry. When either or both are not available, we use Helgeson et al. (1978) fictive solid-solid reaction approximation to estimate S°298 and Cp°₂₉₈
- Log K(T) function is calculated from the thermodynamic function previously selected. It is then compared with solubility data found in previous experiments from the literature
- An additional verification is conducted by drawing the predominance diagram in the chemical sub system of interest for the mineral considered.

The selection results are summarized into Table 3. For each phase, the whole selection process is described into Blanc et al. (2010b). The entire process is not fully described into the present document. However, specific comments are provided, in addition to the values reported in Table 3:

Katoite : for Si substituted hydrogarnets, the selection of LogK₂₉₈ is rather uncertain 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. The problem arises from both the solution experiments and the calorimetric measurements, especially when long reaction times are considered. 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.

Name	Reaction	LogK (1)	LogK (2)	∆fG ⁰ Pr,Tr kJ/mol	∆ _f H⁰ _{Pr,Tr} kJ/mol	S ⁰ Pr,Tr J/mol.K	Cp 25°C J/mol.K	V cm³/mol		
CaO-Al ₂ O ₃ -SiO ₂ -H ₂ O system										
Grossular	$Ca_{3}Al_{2}Si_{3}O_{12} + 12H^{+} = 2Al^{+++} + 3Ca^{++} + 3H_{4}SiO_{4}$		49.35	-6279.46	-6640.00 ª	260.10 ª	326.50 ª	125.28 ª		
Katoite	$Ca_3AI_2(SiO_4)(OH)_8 + 12H^+ = 2AI^{+++} + 3Ca^{++} + 8H_2O + H_4SiO_4$	68.49 (0.8Si)	71.16 ^c	-5433.82	-5907.82	364.00 ^E	415.07 ^E	141.51 ^E		
Straetlingite	Ca ₂ Al ₂ SiO ₂ (OH) ₁₀ :2.5H ₂ O + 10H ⁺ = 2Al ⁺⁺⁺ + 2Ca ⁺⁺ + 10.5H ₂ O + H ₄ SiO 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 ₆ Al ₂ (SO ₄) ₃ (OH ₎₁₂ :26H ₂ O + 12H ⁺ = 2Al ⁺⁺⁺ + 6Ca ⁺⁺ + 38H ₂ O + 3SO ₄	56.80	56.97 d	-15210.23	-17544.53 ^f	1883.59	2174.36 ^g	710.32 ⁱ		
Monosulfoaluminate	Ca₄Al₂(SO₄)(OH)₁₂:6H₂O + 12H⁺ = 2AI⁺⁺⁺ + 4Ca⁺⁺ + 18H₂O + SO₄⁻⁻	72.44	73.07 ^C	-7781.90	-8763.68 ^c	786.94	942.42 ^g	311.26 ⁱ		
Hydrogrossular	Ca ₃ Al ₂ (OH) ₁₂ + 12H ⁺ = 2Al ⁺⁺⁺ + 3Ca ⁺⁺ + 12H ₂ O	80.86	80.32 ^C	-5020.87	-5551.50 ^h	416.61	459.35 ^g	149.52 ª		
C4AH13	Ca ₄ Al ₂ (OH) ₁₄ :6H ₂ O + 14H ⁺ = 2Al ⁺⁺⁺ + 4Ca ⁺⁺ + 20H ₂ O	104.30	103.65 ^c	-7337.63	-8318.00 ^k	685.13	798.90 ^E	269.20 ^j		
Monocarboaluminate	3CaO.Al ₂ O ₃ .CaCO ₃ :10.68H ₂ O + 13H ⁺ = 2Al ⁺⁺⁺ + HCO ₃ ⁻ + 4Ca ⁺⁺ + 16.68H ₂ O	80.56	80.55 ^c	-7269.02	-8175.75 ^f	601.89	730.82 ^E	261.96 ^j		
Hemicarboaluminate	6CaO.2Al ₂ O ₃ .CaCO ₃ .Ca(OH) ₂ :21H ₂ O + 27H ⁺ = 4Al ⁺⁺⁺ + HCO ₃ ⁻ + 8Ca ⁺⁺ + 37H ₂ O	183.47	183.66 ^c	-14685.62	-16600.31	1269.09 ^E	1531.53 ^E	569.02 ^j		
Friedel's salt	2Ca ₂ AI(OH) ₆ CI:2H ₂ O + 12H ⁺ = 2AI ⁺⁺⁺ + 4Ca ⁺⁺ + 2CI ⁻ + 16H ₂ O		74.93 ^c	-6815.44	-7670.04 ^k	527.70	692.86 ^E	276.24 ^j		
	Mg bea	aring phase	es							
Hydrotalcite	$Mg_4AI_2(OH)_{14}:3H_2O + 14H^+ = 2AI^{+++} + 4Mg^{++} + 17H_2O$	73.68	73.74 ^c	-6407.21	-7219.64	512.96 ^E	556.15 ^E	227.36 ^j		
CO3-hydrotalcite	$Mg_4AI_2(OH)_{12}(CO_3):2H_2O + 13H^+ = 2AI^{+++} + HCO_3^- + 4Mg^{++} + 14H_2O$		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 ₄ Fe ₂ (OH) ₁₄ :6H ₂ O + 14H ⁺ = 2Fe ⁺⁺⁺ + 4Ca ⁺⁺ + 20H ₂ O	93.96	95.12 ^c	-6443.63	-7417.40 ^E	705.35 ^E	787.08 ^E	274.40 ^j		
C3FH6	Ca ₃ Fe ₂ (OH) ₁₂ + 12H ⁺ = 2AI ⁺⁺⁺ + 3Ca ⁺⁺ + 12H ₂ O	70.63	72.37 ^c	-4123.57	-4647.59 ^E	436.84 ^E	484.15 ^E	154.50 ^j		
Fe-ettringite	Ca ₆ Fe ₂ (SO ₄) ₃ (OH ₎₁₂ :26H ₂ O + 12H ⁺ = 2Fe ⁺⁺⁺ + 6Ca ⁺⁺ + 38H ₂ O + 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		
Thaumasite										
Thaumasite	CaSiO ₃ .CaSO ₄ .CaCO ₃ :15H ₂ O + 3H ⁺ = 3Ca ⁺⁺ + H ₄ SiO ₄ + SO ₄ + HCO ₃ ⁻ + 10.30 ^q -7559.67 14H ₂ O -7559.67	-8682.04	941.50 ^p	930.00 ^p				329.40		

^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); ^l Moore and Taylor (1970); ^j According to the density provided by Taylor (1997); ^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 selections

Lothenbach et al. (2008) have published a full solubility model for all cement phases, especially based on the experiments of Matschei et al. (2007) and Moschner et al. (2008). In Table 3, we provide a comparison with the LogK₂₉₈ extracted by Lothenbach et al. (2008) from the experiments.

The main differences with those authors arise from the following phases: C3AH6, katoite, C4AH13 and Fe-ettringite:

- C3AH6 : LogK₂₉₈ value retained by Lothenbach et al. (2008), 80.86, is extracted from under saturation experiments. In the present selection, we have preferred a constant extracted from Glasser et al. (1998), 80.32, also based on dissolution experiments, with a 173 days reaction duration, against 84 for Matschei et al. (2007).

- Katoite : the value found by Matschei et al. (2007) is suspected to undergo an incomplete dissolution leading to small value of the equilibrium constant (Blanc et al., 2010b)

- C4AH13: LogK₂₉₈ selected is based on an invariant point whose temperature is 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.

Damidot et al. (2011) have compared the Cem07 database (Lothenbach et al., 2008) with the present work. They 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 a previous work, Damidot and Glasser (1992) predicted a rather similar temperature of 50°C for the appearance of monosulfoaluminate.

5. M-S-H (Magnesium silicate hydrates)

Since (Cole, 1953), magnesium-silicate-hydrate (M-S-H) gels have been reported as resulting from the sulphate attack of concrete in the presence of magnesium ions. More recently, magnesium silicate hydrates (M-S-H) have been observed in slag cement, then synthetized by (Brew and Glasser, 2005) as single phases at the interfaces of cement/rock, which contain soluble magnesium.

M-S-H gels have a variable molar Mg/Si (M/S) ratio \approx 0.75-1.5. At lower M/S ratios M-S-H gel co-exists with amorphous silica and at higher M/S ratios, M-S-H gel rather co-exists with brucite (Bernard et al., 2017; Nied et al., 2016; Roosz et al., 2015; Tonelli et al., 2016). Structural characterization of M-S-H gel by ²⁹Si NMR shows that silicate tetrahedra are dominantly in a layered Q₃ arrangement for all M/S ratios, a structure similar to 7 or 10 Å clay minerals like sepiolite (7 Å) and talc (10 Å).

The difference with natural clay mineral would arise from M-S-H low crystallinity, small particle size and high amount of structural defects (Roosz et al., 2015). Eventually, M-S-H could correspond to proto forms of magnesian 1:1 and 2:1 phyllosilicates like sepiolite, talc or stevensite, structurally different from C-S-H. M-S-H stoichiometry is usually normalised to contain 1 mole of Si.

5.1. CALORIMETRIC MEASUREMENTS ON M-S-H MINERALS

The only available data for M-S-H heat capacity have been measured by Roosz et al. (2018), using a PPMS calorimeter on two synthetic, lyophilized M-S-H gels of measured composition:

 $C^{0}_{p} (Mg_{0.82}SiO_{2.385}(OH)_{0.87}) = 83.13 \pm 5.32 \text{ J/K} \cdot \text{mol}$

C⁰_p (Mg_{1.07}SiO_{2.075}(OH)_{1.99}) = 92.16 ± 5.90 J/K⋅mol

In Roosz et al. (2018), entropy, S_m^0 (J·K⁻¹·mol⁻¹) of each M-S-H gel was then obtained by integration of the $C_{p,m}^0$ data for t = 0.298.15K. It provides directly the entropy of each sample since the authors considered the adsorbed water as not structurally related to the solids:

> S^{0} (Mg_{0.82}SiO_{2.385}(OH)_{0.87}) = 99.76 ± 2.12 J/K·mol S⁰ (Mg_{1.07}SiO_{2.075}(OH)_{1.99}) = 95.94 ± 2.00 J/K·mol

5.2. M-S-H SOLUBILITY

Until recently, solubility datasets were rather scarce for M-S-H hydrates. A first tentative for an equilibrium constant was provided by Dauzères (2010). More recently, Bernard et al. (2017), Lothenbach et al. (2014), Nied et al. (2016) and Roosz et al. (2015) have

performed solution equilibria experiment on synthetic samples with reaction times up to one year and above, and reporting complete solution analyses.

The collection of the solubility data is reported on Figure 8A. Solutions supersaturated with brucite were discarded from the experimental data sets. Temperature seems to influence essentially the dissolved Mg concentrations, with a strong decrease as temperature rises.



Models describing the solubility of magnesium bearing silicates have so far only been developed by Bernard et al. (2017), Nied et al. (2016) and Roosz et al. (2015). Roosz et al. (2015) have proposed a two phases model and Nied et al. (2016) and Bernard et al. (2017) rather developed a solid solution model. The comparison between models predictions and selected experiments is reported in Figure 8B.

From Figure 8B, Bernard et al. (2017) and Nied et al. (2016) models better reproduced the T > 25°C solubility data, while the calculation is carried out at 25°C, which is surprising and the two phase model from Roosz et al. (2018) is rather selected.

Table 4 - Thermodynamic properties of selected M-S-H end members									
Formula	LogK(298 K)	Δ _f G ⁰ kJ/mol	Δ _f H ⁰ kJ/mol	S⁰ J/mol·K	C ⁰ _p (298 K) J/mol⋅K	V ⁰ cm ³ /mol			
Roosz et al. 2018, discrete 2 solid phases model									
Mg _{0.82} SiO _{2.385} (OH) _{0.87} + 0.745H ₂ O + 1.64H ⁺ = 0.82Mg ⁺⁺ + H ₄ SiO ₄ *	9.12 ± 0.20	-1454.25 ± 1.64	-1554.60 ± 1.76	99.76 ± 2.12	83.13 ± 5.32	35.8(*)			
Mg _{1.07} SiO _{2.075} (OH) _{1.99} + 2.14H ⁺ = 1.07Mg ⁺⁺ + 0.065H ₂ O + H ₄ SiO ₄	12.73 ± 0.20	-1739.68 ± 1.71	-1890.20 ± 1.81	95.94 ± 2.00	92.16 ± 5.90	43.0 (*)			

Table 4 Thermodynamic properties of selected MSH and members

^(*) Recalculated consistently with the chemical formula provided by the authors.

6. References

Altmaier, M., Metz, V., Neck, V., Müller, R., Fanghänel, T., 2003. Solid-liquid equilibria of Mg(OH)2(cr) and Mg2(OH)3Cl·4H2O(cr) in the system Mg-Na-H-OH-Cl-H2O at 25°C. Geochimica et Cosmochimica Acta 67, 3595-3601.

Atkins, M., Glasser, F.P., Moroni, L.P., Jack, J.J., 1994. Thermodynamic Modelling of Blended Cements at Elevated Temperatures (50–90 °C). DoE, UK.

Atkinson, A., Hearne, J.A., Knights, C.F., 1989. Aqueous chemistry and thermodynamic modelling of CaO–SiO2–H2O gels. Journal of the Chemical Society, Dalton Transactions, 2371-2379.

Bargar, K.E., Erd, R.C., Keith, T.E.C., Beeson, M.H., 1987. Dachiardite from Yellowstone National Park, Wyoming. The Canadian Mineralogist 25, 475-483.

Benbow, S., Walker, C.S., Savage, D., 2007. Investigating conceptual models for physical property couplings in solid solution models of cement. SKI, Stockholm, p. 38.

Berman, H.A., Newman, E.S., 1963. Heat of Formation of Calcium Aluminate Monosulfate at 25°C. Journal of Research of the National Bureau of Standards. A, Physics and Chemistry 67A, 1-13.

Bernard, E., Lothenbach, B., Rentsch, D., Pochard, I., Dauzères, A., 2017. Formation of magnesium silicate hydrates (M-S-H). Physics and Chemistry of the Earth, Parts A/B/C 99, 142-157.

Berner, U.R., 1988. Modelling the incongruent dissolution of hydrated cement minerals. Waste Management 44/45, 201-219.

Bethke, C., 2004. GWB Reference Manual. RockWare Incorporated.

Blanc, P., Bourbon, X., Lassin, A., Gaucher, E.C., 2010a. Chemical model for cement-based materials: Temperature dependence of thermodynamic functions for nanocrystalline and crystalline C–S–H phases. Cement and Concrete Research 40, 851-866.

Blanc, P., Bourbon, X., Lassin, A., Gaucher, E.C., 2010b. Chemical model for cement-based materials: Thermodynamic data assessment for phases other than C–S–H. Cement and Concrete Research 40, 1360-1374.

Blanc, P., Piantone, P., Lassin, A., Burnol, A., 2006. Thermochimie : Sélection de constantes thermodynamiques pour les éléments majeurs, le plomb et le cadmium. Rapport final.

Brew, D.R., Glasser, F.P., 2005. Synthesis and characterisation of magnesium silicate hydrate gels. Cem. Concr. Res. 35, 85-98.

Buick, I.S., Gibson, R., Wallmach, T., Metz, J., 2000. The occurrence of cuspidine, foshagite and hillebrandite in calc-silicate xenoliths from the Bushveld Complex, South Africa. South African Journal of Geology 103, 249-254.

Chen, J.J., Thomas, J.J., Taylor, H.F.W., Jennings, H.M., 2004. Solubility and structure of calcium silicate hydrate. Cement and Concrete Research 34, 1499-1519.

Chermak, J.A., Rimstidt, J.D., 1989. Estimating the thermodynamic properties (Delta G o f and Delta H o f) of silicate minerals at 298 K from the sum of polyhedral contributions. American Mineralogist 74, 1023-1031.

Clodic, L., Meike, A.-M., 1997. Thermodynamics of Calcium Silicate Hydrates Development of a Database to Model Concrete dissolution at 25°C using the EQ3/6 Geochemical Modeling Code. LLNL, California, p. 67.

Cole, W.F., 1953. A Crystalline Hydrated Magnesium Silicate formed in the Breakdown of a Concrete Sea-wall. Nature 171, 354-355.

Cong, X., Kirkpatrick, R.J., 1996. 29Si MAS NMR study of the structure of calcium silicate hydrate. Advanced Cement Based Materials 3, 144-156.

Courault, A.C., 2000. Simulation expérimentale des C-S-H dans des bétons modernes : étude de la composition et des propriétés à l'équilibre dans des milieux complexes. Université Bourgogne, Dijon, France, p. 201.

Dauzères, A., 2010. Etude expérimentale et modélisation des mécanismes physico-chimiques des interactions béton-argile dans le contexte du stockage géologique des déchets radioactifs. Poitiers, p. 272.

Ederová, J., Šatava, V., 1979. Heat capacities of C3AH6, C4ASH12 and C6AS3H32. Thermochimica Acta 31, 126-128.

Flint, E.P., Wells, L.S., 1934. Study of the system CaO-SiO2-H2O at 30°C and of the reaction of water on anhydrous calcium silicates. Journal of Research of the National Bureau of Standards 12, 751-783.

Fujii, K., Kondo, W., 1981. Heterogeneous equilibrium of calcium silicate hydrate in water at 30 °C. Journal of the Chemical Society, Dalton Transactions, 645-651.

Ghorab, H.Y., Kishar, E.A., Abou Elfetouh, S.H., 1998a. Studies on the Stability of the Calcium Sulfoaluminate Hydrates, Part III: The Monophases. Cement and Concrete Research 28, 763-771.

Ghorab, H.Y., Kishar, E.A., Abou Elfetouh, S.H., 1998b. Studies on the Stability of the Calcium Sulfoaluminate Hydrates. Part II: Effect of Alite, Lime, and Monocarboaluminate Hydrate. Cement and Concrete Research 28, 53-61.

Giffaut, E., Grivé, M., Blanc, P., Vieillard, P., Colàs, E., Gailhanou, H., Gaboreau, S., Marty, N., Madé, B., Duro, L., 2014. Andra thermodynamic database for performance assessment: ThermoChimie. Applied Geochemistry 49, 225-236.

Glasser, F.P., Lachowski, E.E., Macphee, D.E., 1987. Compositional Model for Calcium Silicate Hydrate (C-S-H) Gels, Their Solubilities, and Free Energies of Formation. Journal of the American Ceramic Society 70, 481-485.

Glasser, F.P., Paul, M., Dickson, C.L., Reed, D., 2001. Performance of cement barriers: Experimental and Modelling aspects, pp. 296-311.

Glasser, F.P., Tyrer, M., Quilin, R.D., Pedersen, J., Goldthorpe, K., Bennett, D., Atkins, M., 1999. The chemistry of blended cements and backfills intended for use in radioactive waste disposal. UK Environment Agency, Bristol, UK, p. 332.

Greenberg, S.A., Chang, T.N., 1965. The Hydration of Tricalcium Silicate. The Journal of Physical Chemistry 69, 553-561.

Grutzeck, M., Benesi, A., Fanning, B., 1989. Silicon-29 Magic Angle Spinning Nuclear Magnetic Resonance Study of Calcium Silicate Hydrates. Journal of the American Ceramic Society 72, 665-668.

Helgeson, H., Delany, J., Nesbitt, H., Bird, D., 1978. Summary and Critique of the Thermodynamic Properties of Rock-Forming Minerals. American Journal of Science 278, 1-229.

Helgeson, H.C., 1969. Thermodynamics of hydrothermal systems at elevated temperatures and pressures. American journal of science 267, 729-804.

Helgeson, H.C., Kirkham, D.H., Flowers, G.C., 1981. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes by high pressures and temperatures; IV, Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600 degrees C and 5kb. American Journal of Science 281, 1249-1516.

Houtepen, C.J.M., Stein, H.N., 1976. The enthalpies of formation and of dehydration of some AFm phases with singly charged anions. Cement and Concrete Research 6, 651-658.

Hummel, W., Berner, U., Curti, E., Pearson, F.J., Thoenen, T., 2002. Nagra/Psi Chemical Thermodynamic Data Base 01/01. Universal Publ.

Johnson, C.A., Glasser, F.P., 2003. Hydrotalcite-like minerals (M2Al(OH)6(CO3)0.5.XH2O, where M = Mg, Zn, Co, Ni) in the environment: Synthesis, characterization and thermodynamic stability. Clays and clay minerals 51, 1-8.

Kalousek, G., 1952. Application of differential thermal analysis in a study of the system lime-silicawater, Third international symposium on the chemistry of cement, pp. 296-311.

Keith, T.E., Staples, L.W., 1985. Zeolites in Eocene basaltic pillow lavas of the Siletz River volcanics, central Coast Range, Oregon. Clays and Clay Minerals 33, 135-144.

Kulik, D.A., 2011. Improving the structural consistency of C-S-H solid solution thermodynamic models. Cement and Concrete Research 41, 477-495.

Kusachi, I., Henmi, C., Henmi, K., Afwillite and jennite from Fuka, Okayama Prefecture, Japan. Mineralogical Journal 14, 279-292.

La Iglesia, A., Félix, J.F., 1994. Estimation of thermodynamic properties of mineral carbonates at high and low temperatures from the sum of polyhedral contributions. Geochimica et Cosmochimica Acta 58, 3983-3991.

Lothenbach, B., Matschei, T., Möschner, G., Glasser, F.P., 2008. Thermodynamic modelling of the effect of temperature on the hydration and porosity of Portland cement. Cement and Concrete Research 38, 1-18.

Lothenbach, B., Nied, D., L'Hôpital, E., Achiedo, G., Dauzères, A., 2014. Calcium and magnesium silicate hydrates, in: SCK-CEN (Ed.), 2nd International Symposium on Cement Based Materials for Nuclear Waste (NUWCEM), Avignon (France), p. 12.

Macphee, D.E., Barnett, S.J., 2004. Solution properties of solids in the ettringite—thaumasite solid solution series. Cement and Concrete Research 34, 1591-1598.

Matschei, T., Lothenbach, B., Glasser, F.P., 2007. Thermodynamic properties of Portland cement hydrates in the system CaO–Al2O3–SiO2–CaSO4–CaCO3–H2O. Cement and Concrete Research 37, 1379-1410.

Merlino, S., Bonaccorsi, E., Armbruster, T., 2001. The real structure of tobermorite 11Å normal and anomalous forms, OD character and polytypic modifications. European Journal of Mineralogy 13, 577-590.

Moore, A.E., Taylor, H.F.W., 1970. Crystal structure of ettringite. Acta Crystallographica Section B Structural Crystallography and Crystal Chemistry 26, 386-393.

Myers, R.J., L'Hôpital, E., Provis, J.L., Lothenbach, B., 2015. Effect of temperature and aluminium on calcium (alumino)silicate hydrate chemistry under equilibrium conditions. Cement and Concrete Research 68, 83-93.

Myneni, S.C.B., Traina, S.J., Logan, T.J., 1998. Ettringite solubility and geochemistry of the Ca(OH)2–Al2(SO4)3–H2O system at 1 atm pressure and 298 K. Chemical Geology 148, 1-19.

Newman, E.S., 1956. Heats of formation of xonotlite, hillebrandite, and foshagite. Journal of Research of the National Bureau of Standards 57, 27-30.

Nied, D., Enemark-Rasmussen, K., L'Hôpital, E., Skibsted, J., Lothenbach, B., 2016. Properties of magnesium silicate hydrates (M-S-H). Cement and Concrete Research 79, 323-332.

Nonat, A., 2004. The structure and stoichiometry of C-S-H. Cement and Concrete Research 34, 1521-1528.

Nordstrom, D.K., N., P.L., D., L., E., B., M., M.H., F., J.B., L., P.D., 1990. Revised Chemical Equilibrium Data for Major Water-Mineral Reactions and Their Limitations, Chemical Modeling of Aqueous Systems II. American Chemical Society, pp. 398-413.

Parkhurst, D.L., Appelo, C.a.J., 1999. User's guide to PHREEQC (Version 2) : a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. United States Geological Survey, p. 312.

Perkins, R.B., Palmer, C.D., 1999. Solubility of Ca6[Al(OH)6]2(CrO4)3.26H2O, the chromate analog of ettringite; 5-75°C. APPLIED GEOCHEMISTRY 15, 1203-1218.

Rançon, J.P., 1985. Hydrothermal history of Piton des Neiges volcano (Reunion Island, Indian Ocean). Journal of Volcanology and Geothermal Research 26, 297-315.

Reardon, E., 1990. An ion interaction model for the determination of chemical equilibria in cement/water systems. Cement and Concrete Research 20, 175-192.

Richardson, I., 2014. Model structures for C-(A)-S-H(I). Acta Crystallographica Section B 70, 903-923.

Richardson, I.G., 1999. The nature of C-S-H in hardened cements. Cement and Concrete Research 29, 1131-1147.

Richardson, I.G., 2008. The calcium silicate hydrates. Cement and Concrete Research 38, 137-158.

Rinaldi, R., Sacerdoti, M., Passaglia, E., 1990. Straetlingite; crystal structure, chemistry, and a reexamination of its polytype vertumnite. European Journal of Mineralogy 2, 841-849.

Robie, R.A., Hemingway, B.S., 1995. Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (105 pascals) pressure and at higher temperatures. U.S. G. P. O., Washington and Denver, CO.

Robinson, J., Haas, J., 1983. Heat capacty, relative enthalpy, and calorimetric entropy of silicate minerals: an empirical method of prediction. American Mineralogist 68, 541-553.

Rogers, K.L., Neuhoff, P.S., Pedersen, A.K., Bird, D.K., 2006. CO2 metasomatism in a basalt-hosted petroleum reservoir, Nuussuaq, West Greenland. Lithos 92, 55-82.

Roller, P.S., Ervin, G., 1940. The System Calcium Oxide-Silica-Water at 30°. The Association of Silicate* Ion in Dilute Alkaline Solution. Journal of the American Chemical Society 62, 461-471.

Roosz, C., Grangeon, S., Blanc, P., Montouillout, V., Lothenbach, B., Henocq, P., Giffaut, E., Vieillard, P., Gaboreau, S., 2015. Crystal structure of magnesium silicate hydrates (M-S-H): The relation with 2:1 Mg-Si phyllosilicates. Cem. Concr. Res. 73, 228-237.

Roosz, C., Vieillard, P., Blanc, P., Gaboreau, S., Gaillhanou, H., Braithwaite, D., Montouillout, V., Denoyel, R., Henocq, P., Madé, B., 2018. Thermodynamic properties of C-S-H, C-A-S-H and M-S-H phases: Results from direct measurements and predictive modeling. Applied Geochemistry 92, 140-156.

Sarp, H., Peacor, D.R., 1989. Jaffeite, a new hydrated calcium silicate from the Kombat Mine, Namibia. American Mineralogist 74, 1203-1206.

Savage, D., Walker, C., Arthur, R., Rochelle, C., Oda, C., Takase, H., 2007. Alteration of bentonite by hyperalkaline fluids: A review of the role of secondary minerals. Physics and Chemistry of the Earth, Parts A/B/C 32, 287-297.

Schoenitz, M., Navrotsky, A., 1999. Enthalpy of formation of katoite Ca 2 Al 2 [(OH) 4] 3; energetics of the hydrogarnet substitution. American Mineralogist 84, 389-391.

Smellie, F.P., 2000. Maqarin natural analogue project: Phase IV. SKB, Stocholm, Sweden, p. 163.

Soler, J.M., 2007. Thermodynamic Description of the Solubility of C-S-H Gels in Hydrated Portland Cement. Literature Review. POSIVA, Olkiluoto, Finland, p. 34.

Speakman, K., 1968. The Stability of Tobermorite in the System CaO-SiO2-H2O at Elevated Temperatures and Pressures. Mineralogical Magazine 36, 1090-1103.

Stronach, S.A., Glasser, F.P., 1997. Modelling the impact of abundant geochemical components on phase stability and solubility of the CaO—SiO2—H2O system at 25°C: Na+, K+, SO4 2-, Cl- and CO3 2. Advances in Cement Research 9, 167-181.

Sukheswala, R.N., Avasia, R.K., Gangopadhyay, M., 1974. Zeolites and associated secondary minerals in the Deccan Traps of Western India. Mineralogical Magazine 39, 658-671.

Taylor, H.F.W., 1950. Hydrated calcium silicates. Part I. Compound formation at ordinary temperatures. Journal of the Chemical Society (Resumed), 3682-3690.

Taylor, H.F.W., 1968. The heat of formation of xonotlite, tobermorite, hillebrandite and afwillite, Conference on the Silicate Industry, pp. 179-184.

Taylor, H.F.W., 1997. Cement Chemistry. Thomas Telford, London, UK.

Thomas, J.J., Chen, J.J., Jennings, H.M., Neumann, D.A., 2003. Ca–OH Bonding in the C–S–H Gel Phase of Tricalcium Silicate and White Portland Cement Pastes Measured by Inelastic Neutron Scattering. Chemistry of Materials 15, 3813-3817.

Tonelli, M., Martini, F., Calucci, L., Fratini, E., Geppi, M., Ridi, F., Borsacchi, S., Baglioni, P., 2016. Structural characterization of magnesium silicate hydrate: towards the design of eco-sustainable cements. Dalton Transactions 45, 3294-3304.

Walker, C.S., Savage, D., Tyrer, M., Ragnarsdottir, K.V., 2007. Non-ideal solid solution aqueous solution modeling of synthetic calcium silicate hydrate. Cement and Concrete Research 37, 502-511.

Walker, C.S., Sutou, S., Oda, C., Mihara, M., Honda, A., 2016. Calcium silicate hydrate (C-S-H) gel solubility data and a discrete solid phase model at 25 °C based on two binary non-ideal solid solutions. Cement and Concrete Research 79, 1-30.

Warren, C.J., Reardon, E.J., 1994. The solubility of ettringite at 25°C. Cement and Concrete Research 24, 1515-1524.

Zuern, S.G., Fehr, K.T., 2000. Phase relations and thermodynamic properties of 1.13 nm tobermorite and xonotlite, Sixth International Symposium on Hydrothermal reactions/Fourth International Conference on Solvo-thermal Reactions, pp. 286-289.