# Thermodynamics of Calcium Silicate Hydrates

Development of a Database to Model Concrete Dissolution at 25°C Using the EQ3/6 Geochemical Modeling Code

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1. Introduction

Examination of the ability to model aqueous systems of interest to the repository proposed by the Yucca Mountain Project has revealed an historical deficit in the ability to model complex water–material systems that contain ordinary Portland cement (OPC) at elevated temperature (e.g., Bruton et al., 1994; Meike et al., 1994). One of the reasons is that cement chemistry typically concentrates on two issues of importance to the concrete industry: the hydration of cement powder, which contains reactive phases that do not persist in the cured concrete, and the causes of mechanical degradation at earth surface temperatures such as delayed ettringite formation and alkali silica reaction. Such modeling capability is not available in the open literature, even from applications that might have developed high temperature approaches, such as deep drilling for oil and geothermal resource recovery. The ability to simulate the interaction between concrete, as it evolves over time, and water has become more critical as repository designers begin to consider the incorporation of OPC materials in the emplacement drifts. The Yucca Mountain Project is unique among the high-level radioactive waste repository projects in the world in terms of the need to understand and predict processes in excess of 100°C (see, e.g., Meike, 1997). Our aim has been to develop this capability in the area of aqueous chemistry.

Several important studies have been aimed at modeling OPC–water interactions at room temperature and at elevated temperatures to 90°C. In this report, we discuss the incorporation of data from the literature into our chemical modeling databases. During the lifetime of this project, it has been our intention to interface the existing knowledge at room temperature to 90°C with new data that will allow us to discuss effects at elevated temperatures. Fundamental to that goal is developing a seamless database of thermodynamic and kinetic properties of the phases of interest. These properties include solubilities, heats of formation, and heat capacities, which must be examined in detail to determine potential sources of error. Our attempt to measure new thermodynamic data for the relevant phases and temperatures and the consequent incorporation of those data into our databases is not addressed in this report.

Our purpose in the first phase of this work has been to use data available from the literature to build the most robust database possible and to test it at room temperature. The room temperature test is a necessary preliminary to planned tests at elevated temperatures, which are not included in this report. The new database has been constructed to interface with the EQ3/6 geochemical code (Wolery, 1992a). This objective has been achieved by building progressively more complex databases from a chemically simple three-component system, with additional single-component increments. Each increment is tested for internal consistency, and for the ability to simulate relevant experimental data from the literature. Another objective was to compare the robustness of various extant databases, translated into a format that could be used by our chemical codes, by running the same simulation with different databases, as the capabilities of the database would allow (see the discussion of EQ3/6 and databases below). This report describes progress during the first phase.

In the process of working in this area, it is necessary to be conversant in the symbols used by both cement chemistry and standard chemistry (see Appendix A for a summary). The symbolism of both fields is used in this report. For an expanded lexicon of cement chemistry notation, refer to Taylor (1990).

2. Data Availability and Modeling Cementitious Materials

Of the major reactant phases of cement powder—alite, belite, possible residual glass, gypsum, and ferrite [$C_2(A,F)$] (see Appendix A for standard cement formula nomenclature)—only the thermochemical data for gypsum are essentially complete. Knowledge of the energetic data for these phases, however, is not required for our purposes. It is only necessary to model the hydration and curing of concrete. Our goal is to model the interaction between water and well cured concrete, some of which may have undergone extensive transformation in the solid state due to a thermal pulse. Below we review the phases of interest, determined by their observation in experiment and natural and historical analogs that have experienced the conditions of interest.

Most of the hydrous phases of cured cement and the anhydrous and hydrous solid solutions lack calorimetric data. The kinetics of transformation of C-S-H into other phases at its upper temperature limit are significant to predictions of cement behavior in the repository, which will stay at 80°–120°C for an extended time. Of prime importance for 25°C performance modeling are calorimetric data for ettringite and tobermorite and well-characterized solid solutions of these phases. The prediction of chemical reactions at greater temperatures requires more data than is presently available. Geochemical codes are also useful in the absence of these data for conducting a sensitivity analysis to determine the solid solutions or end-member phases that are critical for calorimetry. The original ΔH of formation (20°C) from CaO, and silica-gel thermodynamic data for all Ca_2SiO_4 phases, are evaluated by Haas et al. (1981). Qualitative rate information has been obtained for ettringite components (Majling et al., 1985). Other than an enthalpy of dehydration (Maycock et al., 1974) and C_p data (Ederova and Satava, 1979) obtained over the range of 273 to 333 K, thermochemical data for ettringite are calculated (Sarker et al., 1982; Babushkin et al., 1985). The only experimental data for "monosulfate" (C_4ASH_{12}) located to date is C_p data from 273 to 353 K (Ederova and Satava, 1979). As discussed previously, the kinetics of the relevant reactions are even less well understood.

Comparisons of cement leachates with calculations performed using available data and standard thermochemical tables (Barnes and Roy, 1983) suggest the best agreement with the solutions buffered by tobermorite and possibly gyrolite. Calculated activity products have been compared with pure C_3S, and with experimentally obtained solution compositions (Ca^{++}, Na^+, K^+, pH, and $SO_4^=$, but not Al or $CO_3^=$) from cement hydrated for up to 3 hr (Gartner et al., 1985). The comparisons suggest that although no difference in supersaturation was observed with respect to portlandite, gypsum, and syngenite [$CaK_2(SO_4)_2\cdot H_2O$], thermodynamic equilibrium is not achieved during early hydration (Moragues et al., 1987, 1988), and high ionic concentrations of the solutions cause departure from Debye-Hückel theory. The most successful chemical models to date have been achieved by working with a limited number of equations that include C-S-H solid solutions, monosulfate solid solution, and ferrite solid solution. Glasser et al. (1985) analyze a simplified cement system as the ternary CaO–SiO_2–H_2O. Barret and Bertrandie (1986) make a similar analysis of the system CaO–Al_2O_3–CO_2–H_2O. Incorporation of aggregate into repository concrete will increase the complexity of geochemical modeling. Calculations that include Portland cement, special cements, and concretes that incorporate bfs, fly ash, and silica fume (Berner, 1987) have achieved some success for equilibrium-solid-phase and pore-solution-composition data obtained from experiment, but they do not readily take reaction progress into account.

The use of numerical simulations to integrate the effects of the variables complements experimental and historical investigations. Eventually, coupled chemical effects that are

difficult or inaccessible through experiment can be examined. However, even the present chemical data base (Sarker et al., 1982; Babushkin et al., 1985), although limited, can be manipulated to obtain insight into some effects that may be expected due to man-made materials. Conversely, the data base will be enhanced over time by incorporation of new thermodynamic data from the experimental and historical investigations.

3. Selected Room-Temperature Cement Models

3.1 C–S–H Gel Models

Calcium silicate hydrate (C–S–H) is the major constituent of a cement paste and is characteristically poorly crystalline or nearly amorphous in a young cement paste. C–S–H can also be synthesized by reaction between $Ca(OH)_2$ and silicic acid, or between solutions of sodium silicate and a soluble calcium salt. In this manner, quasi-crystalline varieties can be obtained. Two of them, known as C–S–H(I) ($0.8 < Ca/Si < 1.3$) and C–S–H(II) ($Ca/Si > 1.5$), can be compared structurally to tobermorite and jennite, respectively. The relation between this important conceptual step and its thermodynamic significance has been discussed by Jennings (1986) and Gartner and Jennings (1987).

From numerous values collected in the literature (see, e.g., Atkins et al., 1991, Atkinson et al. 1989, 1990; Berner, 1988, 1990; Glasser et al., 1987a; Fujii and Kondo, 1983; Table 1) and for calcium and silica concentrations in the aqueous phase in contact with the gel, the authors established that the compositions cluster around one of two curves, corresponding respectively to two different C–S–H structures. The points that cluster about one curve correspond to C–S–H gel prepared from $Ca(OH)_2$ and silicic acid, by mixing solutions of sodium silicate and a soluble calcium salt, or by complete hydration of C_3S. The structure of these gels can be associated with C–S–H(I), which is structurally related to tobermorite. The other curve represents analyses of samples obtained by incomplete hydration of C_3S or C_2S. It has been proposed that these gels are a mixture of stacked sheets of tobermorite-like and jennite-like units of C–S–H (Taylor, 1950). Most of the thermodynamic and compositional models found in the literature are developed assuming the existence of solid solutions. Jennings also developed a model to calculate the Ca/Si ratio of this gel as a function of the thermodynamic properties of the aqueous phase, with which it is in equilibrium.

Table 1.   Experimental compositions investigated by selected authors [a]

Ca/Si	$0 \leq Ca/Si \leq x_1$ [a]	$x_1 \leq Ca/Si \leq 2.0$
Atkinson et al. (1989, 1990)	C–S–H with Ca/Si = 0.8 + amorphous SiO_2	C–S–H with Ca/Si = 0.8
Berner (1988, 1990)	C–S–H with Ca/Si = 1.0 + amorphous SiO_2	C–S–H with Ca/Si = 1.0 + $Ca(OH)_2$
Fujii and Kondo (1983)		Tobermorite-14Å (Ca/Si = 0.833) + $Ca(OH)_2$
Glasser et al. (1987a) Atkins et al. (1991)	$Ca_xH_{6-2x}Si_2O_7 \cdot nH_2O$	$Ca_xH_{6-2x}Si_2O_7 \cdot nH_2O + mCa(OH)_2$

[a] $x_1 = 0.8$ for Atkinson et al., 1.0 for Berner, and 0.833 for Fujii and Kondo.

3.2 Composition of C–S–H Gel as a Function of Alkali Concentration

During the hydration (hardening) of real cement pastes, the interaction between C–S–H gels and other chemical components—in particular, alkalis—also affects their composition. Unhydrated Portland cement may contain up to 3% by weight of alkali oxides and can affect the ultimate composition of the hardened cement paste. The alkali oxides take the form of sulfates (or calcium alkali sulfates) or as part of the clinker phases. The solubility of these phases affects the composition of the pore fluid. After hydration, much of the alkalis appear in the pore fluid, which has a substantial effect on the Ca^{+2} concentration compared to that of the pure $CaO–SiO_2–H_2O$ system. This affects the morphology and composition of the C–S–H

gel. According to Suzuki et al. (1985), the high solubility of sodium allows young Na-bearing C–S–H gels to converge on the same solubility values as the Na-free C–S–H gels. Solubility, chemistry, and aging of calcium silicate hydrates in alkaline solutions are also discussed by MacPhee et al. (1989), Glasser et al. (1985), and Damidot et al. (1994).

Alkalis are retained in the solid hydration products, notably C–S–H gels, to a lesser extent. However, even small concentrations can modify their solubility products significantly. Experiments using C–S–H prepared from lime and silicic acid in a sodium or potassium hydroxide solution, and from C_3S hydration in a sodium hydroxide solution (Atkins et al., 1991), have shown that the composition of the gel is modified by the uptake of alkalis, which results in different solubility properties compared to the unmodified gels. This observation has led to the development of a model representing the uptake of Na by C–S–H gel, using a surface adsorption model. The Berner-type model (see discussion below) has been modified (Atkins et al., 1992) empirically to take into account this influence of alkali on C–S–H thermodynamic behavior.

3.3 Cement Degradation or Aging Models

Table 2 compares the database codes and sources of two well-recognized models for cement–water interaction. Two major models have been selected among the different approaches found in the literature. They have been developed, respectively, by Berner (1987, 1988, 1990) and Atkins et al. (1992)–Bennett et al. (1992), where the two latter references carry on the methods of Glasser et al. (1987a, b). Table 3 shows the similarities between the two studies. Table 4 lists the dissociation reactions favored by many of the models.

Table 2.   Sources of the Berner (1987, 1988, 1990) and Glasser et al. (1987a, b) models

	Berner (1987, 1988, 1990)	Glasser et al. (1987a, b)
Experimental data used to build and fit the model	Flint and Wells (1934) Fujii and Kondo (1981) Greenberg and Chang (1965) Kalousek (1952) Roller and Ervin (1940) Taylor (1950)	Fujii and Kondo (1981, 1983) Greenberg and Chang (1965) Roller and Ervin (1940) Suzuki et al. (1985)
Code used for modeling	MINEQL	Not identified in references cited
Database used for aqueous species	MINEQL and PHREEQE	Sillen and Martell (1964) Babushkin et al. (1985)

Table 3. Selected aspects of the Berner (1987, 1988, 1990) and Atkins et al. (1992)—
Bennett et al. (1992) models

	Berner (1987, 1988, 1990)	Atkins et al. (1992)—Bennett et al. (1992)
System	CaO–Al$_2$O$_3$–SiO$_2$–MgO–SO$_3$–H$_2$O	CaO–Al$_2$O$_3$–SiO$_2$–MgO–SO$_3$–H$_2$O
Solid phases	portlandite	portlandite
		gypsum
		silica gel
		gibbsite or bayerite
	brucite	brucite
	C$_3$AH$_6$–C$_3$FH$_6$	hydrogarnet
		C$_4$AH$_{13}$
	C$_x$SH$_x$, x < 1.8	C-S-H gel
		tobermorite
	hydrotalcite	hydrotalcite
		siliceous hydrogarnet
	ettringite	ettringite
	AFm phase	monosulphate AFm
		gehlenite hydrate
	calcite	
	NaOH, KOH	
Code		PHREEQE
Database	MINEQL	Subset of CHEMVAL
	PHREEQE (Parkhurst et al., 1980)	(Read, 1991)
C–S–H thermodynamic treatment	Berner's model	Adaptation of Berner's model
Validation of the model	Degradation of cement in natural marl groundwater	Series of pore-fluid analyses from 5-yr-old pastes

Table 4.   Dissociation reactions of several models

Solid Phases	Formula	Dissociation Reaction	Log K_{sp}	Ref.
Portlandite	$Ca(OH)_2$	$Ca^{+2} + 2 H_2O - 2 H^+$	22.67	a, b
Gypsum	$CaSO_4 \cdot 2H_2O$	$Ca^{+2} + SO_4^{-2} + 2 H_2O$	–4.34	a, b
Amorphous SiO_2	SiO_2	$H_4SiO_4 - 2 H_2O$	–1.46	a, b
Quartz	SiO_2	$H_4SiO_4 - 2 H_2O$	–3.95	a, b
Chalcedony	SiO_2	$H_4SiO_4 - 2 H_2O$	–3.52	a, b
Gibbsite	Al_2O_3	$Al^{+3} + 3 H_2O - 3 H^+$	8.05	a, b
Brucite	$Mg(OH)_2$	$Mg^{+2} + 2 H_2O - 2 H^+$	16.74	a, b
Grossular	$Ca_3Al_2(SiO_4)_3$	$3 Ca^{+2} + 2 Al^{+3} + 3 H_4SiO_4 - 12H^+$	57.21	a, b
Talc	$Mg_3Si_4O_{10}(OH)_2$	$3 Mg^{+2} + 4 H_4SiO_4 - 4 H_2O - 6 H^+$	19.58	a, b
Kaolinite	$Al_2Si_2O_5(OH)_4$	$2 Al(OH)_4^- - 2 H_4SiO_4 + 2 H^+ - 7 H_2O$	–36.92	a, b
Halloysite	$Al_2Si_2O_7 \cdot 2H_2O$	$2 Al^{+3} - 2 H_4SiO_4 + H_2O - 6 H^+$	10.45	a, b
Chabazite	$CaAl_2SiO_4O_{12} \cdot 6H_2O$	$Ca^{+2} + 2 Al^{+3} + 4 H_4SiO_4 + 2 H_2O$	13.63	b
Ettringite	$Ca_6Al_2S_4O_6(OH)_{12}$	$6 Ca^{+2} + 2 Al^{+3} + 3 SO_4^{-2} + 12 H_2O - 12 H^+$	57.66	b
Hydrogarnet	$Ca_3Al_2O_6 \cdot 6H_2O$	$6 Ca^{+2} + 2 Al^{+3} + 12 H_2O - 12 H^+$	82.57	b
Tobermorite	$Ca_5Si_6O_{17} \cdot 5H_2O$	$5 Ca^{+2} + 6 H_4SiO_4 - 10 H^+ - 2 H_2O$	65.05	b
Hydrotalcite	M_4AH_{10}	$4 Mg^{+2} + 2 Al^{+3} + 17 H_2O - 14 H^+$	73.78	b
Gehlenite hydrate	$Ca_2Al_2SiO_7 \cdot 8H_2O$	$2 Ca^{+2} + 2 Al^{+3} + H_4SiO_4 + 11 H_2O$	49.67	b
SiO_2 (Berner)		$H_4SiO_4 - 2 H_2O$	—	c
CaH_2SiO_4 (Berner)		$Ca^{+2} + H_2SiO_4^{-2}$	—	c
$Ca(OH)_2$ (Berner)		$2 Ca^{+2} + 2 H_2O - 2 H^+$	—	c

[a]   Read (1991)
[b]   Atkins et al. (1992)
[c]   Berner (1987, 1988, 1990) C–S model

3.3.1 Berner-Type Model

Three submodels have been developed by Berner (1988, 1990). These are for cement hydration, the thermodynamic properties of C–S–H, and the degradation of hydrated cement in natural groundwaters. The hydration model, after the calculation of the clinker's phase assembly (after the method of Bogue, 1929), considers the hydration of each clinker mineral independently, with fitted parameters. The possible hydration products are restricted to a few characteristic groups, and the blending agents are assumed to react completely. The C–S–H thermodynamic model is discussed above. With respect to degradation in contact with an aqueous medium, a mixing tank model has been developed, taking into account the following solid phases: C–S–H gel, KOH, NaOH, $Mg(OH)_2$ and portlandite. During an exchange cycle, a certain volume of groundwater is equilibrated with these solid phases, then removed from the system, and replaced by a fresh volume. Berner defines the "lifetime" of the cement as the number of cycles required to dissolve the C–S–H gel completely.

3.3.2 Model of Atkins et al.: CEMCHEM

Atkins et al. (1992) have developed a thermodynamic model (CEMCHEM) for cements (OPC or blended OPC) whereby, given the formulation specifications, the composition of the solid phases and the pore fluid are calculated in the mature paste at 25°C. This program is intended to be a precursor to computer codes, such as PHREEQE, MINEQL, or EQ3/6 for use in modeling the near-field chemistry. See INTERA Environmental Consultants, Inc. (1983, p. 114) for a comparison of PHREEQE and EQ3/6.

An internally consistent thermodynamic database (CEMENT) has also been developed by Atkins et. al. (1992) for use with CEMCHEM. It is mainly composed by a subset of the CHEMVAL database, some data from the U.S. Geological Survey database, as well as the thermodynamic data for "Berner's phases": CaH_2SiO_4, SiO_2, and $Ca(OH)_2$, constituting the ending members of the solid solutions for the C–S–H model. Data obtained by Atkins et al. (1992) from solubility experiments were also added to the list, corresponding to the phases known to be stable, or at least metastable, in the cement system at ambient temperatures.

This package can apparently be used easily as a premodel for speciation codes to simulate the degradation of cement pastes.

4. The EQ3NR/EQ6 Modeling Code and Associated Databases

The EQ3NR/EQ6 software package (Wolery 1992a, 1992b; Wolery and Davelier, 1992) com–prises three executable programs (EQPT, EQ3NR, and EQ6) and several databases that are used at the modeler's discretion (Figure 1). EQPT, which formats databases to be readable by EQ3NR and EQ6, is not shown in Fig. 1. The input file for EQ3NR contains the analytical composition of a solution (including total concentrations of dissolved components, pH, Eh, and oxygen fugacity). The code calculates the distribution of chemical species using thermo-dynamic data located in the selected database. The output is an output file and a pickup file, which is used to initialize the EQ6 input file. EQ6 models the reaction of the aqueous solution with a set of minerals and gases, as well as fluid-mixing and temperature changes.
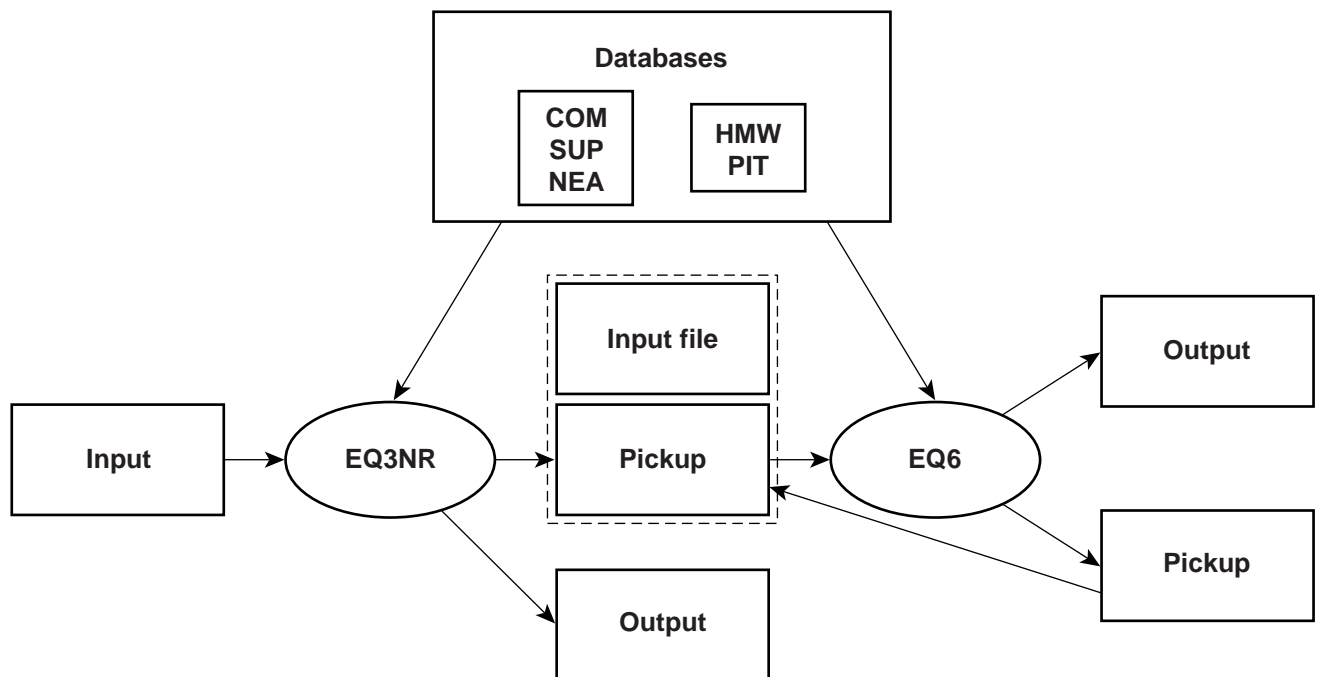
Figure 1. Schematic diagram of the flow of information among EQ3NR, EQ6, the databases, and the input and output files

Five database files are now available for use with EQ3/6. Three of these (COM, SUP, and NEA) may be used with either of the two activity coefficient options in EQ3/6 that are designed for dilute solutions—i.e., the Davies equation or the B-dot equation (Wolery, 1992a, b; Wolery and Daveler, 1992)—to calculate the activity coefficients. In general, the use of these two options is restricted to geochemical solutions that have stoichiometric ionic strengths less than that of seawater (i.e., ≤ 0.7 molal; Garrels and Christ, 1965). The two other data files (HMW and PIT) use the Pitzer (1979) equations and are suitable for modeling high-concentration solutions. The salient features of each database, summarized in Table 5, are:

- **COM database.** This dataset represents a melange of data found in the SUP and NEA datasets. Other data in this database have been obtained by correlation or interpola-tion, so this set offers the least assurance of internal consistency. However, it is the only means available to model problems with high compositional complexity.

- **SUP database.** Based entirely on the SUPCRT92 program (Johnson et al., 1992), this database has a high level of internal consistency. The database covers a wide range of chemical species but does not contain many data related to C–S–H species that might be formed in cements at temperatures between 60° and 300°C.

- **NEA database.** This database was produced by the Data Bank of the Nuclear Energy Agency of the European Community (Grenthe et al., 1989) and is specifically tailored to conduct uranium studies.

- **HMW database.** This dataset is based on the use of Pitzer's activity coefficient expressions that were used by Harvie, Moller, and Weare (1984) to model the solubility of geochemically significant components (Harvie and Weare, 1980). It can be applied to both dilute solutions and concentrated brines at 25°C. Where appropriate data exist, it can be extended to elevated temperatures. It is consistent with stability data and most mean molal activity coefficient measurements, but it only treats the components present in the "sea–salt–water" system. Elements important to modeling of cement in a geologic repository, such as Al and Si, are not included in this database. This dataset is not appropriate for extrapolation outside the compositional space defined by the regressions, nor can it be used in conjunction with other thermodynamic and activity coefficient models because ΔG_f° (the standard state free energy of formation) is a regression term in this case.

- **PIT database.** The PIT database is based primarily on data summarized by Pitzer (1979). This data file was intended to be applied to some concentrated brines between 25° and 100°C. Application of this database to include higher temperature data would require a revision since it is based on truncated Taylor series. It covers a larger set of species than the HMW database, but it does not address the silica and inorganic carbon species that are necessary to model cement in a geologic repository. In addition, it contains some internal inconsistencies.

Table 5.   Databases available for use with the EQ3NR/EQ6 software package

Database	Description	Formalism
COM	Composite data set	Extended
SUP	SUPCRT 92	Debye–Hückel
NEA	–	Davies
		B-dot
HMW	Harvie, Moller, and Weare	Pitzer
PIT	Pitzer	Pitzer

The thermodynamic databases that are presently available for use with EQ3/6 do not contain some of the thermodynamic information necessary for modeling the cementitious systems in a natural environment (e.g., Bruton et al., 1994; Meike et al., 1994). Our aim has been to develop that capability through several steps. Our first step is to incorporate extant databases developed for other cement specific (and chemically limited) modeling packages into one of the present geologically oriented databases for EQ3/6. The next step is to acquire new thermodynamic data and, through the necessary iterations, develop the database necessary for addressing rock–concrete–water evolution through time. The objective has been to develop three different types of databases that would reflect stages of maturity in the ability to model systems that contain OPC and aspects of our ability to assess our modeling capabilities in comparison with other models in the literature. The three types of databases are:

- **Database 1.** Three datasets for the Ca–Al–Si–S–Mg–H_2O system have been assembled by Atkins et al. (1991, 1992, and 1994) for temperatures of 25°, 50°, and 90°C. These datasets describe almost completely the available data for the composition of minerals in a cement system at these temperatures. A database file compatible with the EQ3/6 software package will be developed from these data to test the reproducibility of the simulations obtained using the codes used by Atkins et al. (1991, 1992, and 1994), namely MINEQL and PHREEQE.

- **Database 2.** This database originates with a geochemical database. However, it is first purged of all the chemical elements outside of the system CaO–SiO_2–Al_2O_3–MgO–SO_3–Na_2O–K_2O–H_2O. New minerals relevant to hydrothermally altered concrete are added, one after another, and the results are compared against available data in the literature.

- **Database 3.** This database originates with the geochemical database. New minerals relevant to hydrothermally altered concrete are added, one after another, and the results are compared against available data in the literature.

The present report represents progress in the development of these databases.

4.1 Building a Database Compatible with EQ3/6

Several software tools are needed to build a database that can interact with EQ3/6. These are included in a database known as GEMBOCHS. Two programs are used to interact with the GEMBOCHS database and software library (Johnson and Lundeen, 1994). JEWEL is a graphical user interface. Up-to-date versions of a data file can be generated for the conditions of interest. Customized versions of these data files can also be created from one of the standard datasets, from a few species subset, from the bulk system composition, or from any combination thereof. FACET is a tool developed to consult with and select species from the GEMBOCHS database. It is also used to add new data for the creation of a database with a specific purpose. Our present exercise is not to modify the official GEMBOCHS database, but to use the same tools to create our own set of databases that will provide the dialog necessary to set that process into motion, only as necessary.

5. Initial State of the SUP Database

The SUP database is based entirely on SUPCRT92 (Johnson et al., 1992) and has a high level of internal consistency among the standard thermodynamic data. This file also covers a wide range of chemical elements and chemical species, including some organic species, most of which have a small carbon number. Table 6 lists the species present in the SUP data file.

Table 6.   Chemical elements present in the SUP data file

O	Cd	Fe	In	Na	Rn	Sr
Ag	Ce	Ga	K	Nd	Rb	Tb
Al	Cl	Gd	Kr	Ne	Re	Tl
Ar	Co	H	La	Ni	Rn	Tm
Au	Cr	As	Li	Pb	S	V
B	Cu	C	Lu	Pd	Sc	W
Ba	Dy	P	Mg	Pr	Se	Xe
Be	Er	He	Mn	Ra	Si	Y
Br	Eu	Ho	Mo	Rb	Sm	Yb
Ca	F	I	N	Re	Sn	Zn

However, as is the case with most of the standard databases, SUP does not contain the key cement phases—in particular, the crystalline calcium silicate hydrates. This is due mainly to the lack of reliable thermodynamic data for these minerals. Furthermore, some of these cement minerals may dissolve incongruently, which cannot be described through a simple solubility product, but requires the development of more elaborate solubility models. The more elaborate models can be incompatible with the SUP database structure. This and other idiosyncrasies of the SUP database and the state of the database development software at the time our work was conducted (1995–96) have controlled some aspects of the manner in which our new databases have been developed (see the discussion below). As new capabilities are developed in database development software, other, more-efficient strategies for the development of databases than the one that was used here may be possible. Available data for most of these minerals are included in the COM database. (Recall that this database contains more data than the SUP data file, but these data are less internally consistent.) Table 7 and Table 8 list the minerals and relevant data for the COM database.

Table 7. Cement-related minerals present in the COM data file: composition, dissociation reaction, and solubility products

Mineral	Composition	Aqueous Dissociation Reaction	Log K (°C)							
			0°	25°	60°	100°	150°	200°	250°	300°
Afwillite	$Ca_3Si_2O_4(OH)_6$	Afw. + 6 H^+ + 2 $SiO_{2(aq)}$ + 3 Ca^{+2} + 6 H_2O	64.93	60.05	54.10	48.57	47.12	38.81	35.24	32.11
C_4AH_{13}	$Ca_4Al_2O_7{:}13H_2O$	C_4AH_{13} + 14 H^+ + 2 Al^{+3} + 4 Ca^{+2} + 20 H_2O	—	105.54	—	—	—	—	—	—
C_4AH_{19}	$Ca_4A_{l2}O_7{:}19H_2O$	C_4AH_{19} + 14 H^+ + 2 Al^{+3} + 4 Ca^{+2} + 26 H_2O	—	101.97	—	—	—	—	—	—
CAH_{10}	$CaAl_2O_4{:}10H_2O$	CAH_{10} + 8 H^+ + 2 Al^{+3} + Ca^{+2} + 14 H_2O	—	36.28	—	—	—	—	—	—
C_2AH_8	$Ca_2Al_2O_5{:}8H_2O$	C_2AH_8 + 8 H^+ + 2 Al^{+3} + Ca^{+2} + 14 H_2O	—	57.86	—	—	—	—	—	—
Ettringite	$CaAl_2(SO_4)_3(OH)_{12}{:}26H_2O$	Ettr. + 12 H^+ + 2 Al^{+3} +3SO_4^{-2} + 6 Ca^{+2} + 38 H_2O	67.00	60.81	54.70	50.28	47.14	45.43	—	—
Gyrolite	$Ca_2Si_3O_7(OH)_2{:}1.5H_2O$	Gyr. + 4 H^+ + 2 Ca^{+2} + 3 $SiO_{2(aq)}$ + 4.5 H_2O	23.95	22.91	21.17	19.40	17.63	16.24	15.08	14.02
Foshagite	$Ca_4Si_3O_9(OH)_2{:}5H_2O$	Fos. + 8 H^+ + 4 Ca^{+2} + 3 $SiO_{2(aq)}$ + 5.5 H_2O	71.40	65.92	59.08	52.62	46.18	41.04	36.75	32.95
Gypsum	$CaSO_4{:}H_2O$	Gyps ' SO_4^{-2} + Ca^{+2} + 2 H_2O	−4.53	−4.48	−4.61	−4.90	−5.43	−6.13	−7.04	−8.30
Hillebrandite	$Ca_2SiO_3(OH)_2{:}0.17H_2O$	Hil. + 4 H^+ + 2 Ca^{+2} + $SiO_{2(aq)}$ + 3.17 H_2O	39.98	36.82	33.02	29.49	26.02	23.25	20.95	18.93
Monohydro-talcite	$CaCO_3{:}H_2O$	Mon. + H^+ + Ca^{+2} + HCO_3^- + H_2O	3.01	2.68	2.31	1.98	1.66	1.37	—	—
Okenite	$CaSi_2O_4(OH)_2{:}H_2O$	Oken. + 2 H^+ + Ca^{+2} + 2 $SiO_{2(aq)}$ + 3 H_2O	10.54	10.38	9.95	9.57	9.35	9.35	—	—
Portlandite	$Ca(OH)_2$	$Ca(OH)_2$ + 2 H^+ + Ca^{+2} + 2 H_2O	24.62	22.56	20.20	18.06	15.97	14.31	12.94	11.75
Toberm.-9Å	$Ca_5Si_6H_6O_{20}$	Tob-9 +10 H^+ + Ca^{+2} + 6 $SiO_{2(aq)}$+ 8 H_2O	73.76	69.08	62.56	56.18	49.75	44.59	40.25	36.29
Toberm.-11Å	$Ca_5Si_6H_{11}O_{22.5}$	Tob-11 +10 H^+ + 5 Ca^{+2} + 6 $SiO_{2(aq)}$+ 10.5 H_2O	69.63	65.61	59.91	54.32	48.74	44.33	40.67	37.34
Toberm.-14Å	$Ca_5Si_6H_{21}O_{27.5}$	Tob-14 + 10 H^+ + 5 Ca^{+2} + 6 $SiO_{2(aq)}$ + 15.5 H_2O	67.03	63.84	59.26	54.89	50.74	47.64	45.16	42.89
Xonotlite	$Ca_6Si_6O_{17}(OH)_2$	Xon. +12 H^+ + 6 Ca^{+2} + 6 $SiO_{2(aq)}$ + 7 H_2O	99.26	91.83	82.41	73.71	65.41	59.15	—	—
Wollastonite	$CaSiO_3$	$CaSiO_3$ + 2 H^+ + Ca^{+2} + $SiO_{2(aq)}$ + H_2O	14.88	13.76	12.27	10.83	9.37	8.20	7.21	6.31

Table 8. Cement-related minerals present in the COM data file: extrapolation algorithm, thermodynamic data used for the calculations, and corresponding bibliographic references

Minerals	Extrapolation Algorithm	ΔG^0_{f298} (Kcal/mole)	ΔH^0_{f298} (Kcal/mole)	S^0_{PrTr} (cal/mole/K)	Source	T^0 (cal)	T^1 (cal)	T^{-2} (cal)	T_{limit} (°C)	Source
Afwillite	C_p integration	−1052.95	−1143.20 −1143.31	74.60	a	81.54	45.1×10^{-3}	-1.47×10^6	626.85	b
C_4AH_{13}		−1749.00	N/A	N/A	a					
C_4AH_{19}		−2094.00	N/A	N/A	a					
CAH_{10}		−1107.00	N/A	N/A	a					
C_2AH_8		−1153.00	N/A	N/A	a					
Ettringite	c.e.a. [1]	−3628.43	−4193.00	427.80	a					
Gyrolite	C_p integration	−1085.65	−1175.85 −1176.54	64.00	a	79.47	3.63×10^{-2}	-1.76×10^6	726.85	b
Foshagite	C_p integration	−1347.90	−1438.26	78.95	a	87.95	3.95×10^{-2}	-1.35×10^6	726.85	b
Gypsum	C_p integration	−1797.20 kJ/mol	−2022.63 −2022.68 kJ/mol	194.14 J/mol/K	c	21.84	7.6×10^{-2}		526.85	b
Hillebrandite	C_p integration	−592.90	−637.15 −637.40	38.40	a	41.04	2.24×10^{-2}	-0.74×10^6	626.85	b
Monohydro-talcite	c.e.a. [1]	−1361.60 kJ/mol	−1498.29 kJ/mol	129.83 J/mol/K	c					
Okenite	c.e.a. [1]	−686.40	−749.64	40.90	a					
Portlandite	C_p integration	−898.41 kJ/mol	−986.07 kJ/mol	83.39 J/mol/K	c	186.67 J	-0.22×10^{-1} J	-0.16×10^4 J	426.85	c
Toberm.-9Å	C_p integration	−2215.00	−2375.00 −2375.41	122.65	d	143.55	0.747×10^{-1}	-2.08×10^6	726.85	d
Toberm.-11Å	C_p integration	−2361.45	−2556.30 −2556.41	146.15	a	110.6	0.19		726.85	d
Toberm.-14Å	C_p integration	−2647.30	−2911.25 −2911.35	193.15	a	132.2	0.17		726.85	d
Xonotlite	c.e.a. [1]	−2259.40	−2396.70 −2397.24	121.30	a					
Wollastonite	SUPCRT92	−369.22	−389.59	19.60	e	26.64	0.36×10^{-2}	-0.652×10^6	1126.85	e

Sources: a) Sarker et al., 1982; b) Barin et al., 1977; c) Robie et al., 1979; d) Barin and Knacke, 1973; e) Johnson, 1992. [1] c.e.a. = constant enthalpy approximation

Uncertainty in the thermodynamic values originates from several sources. First, an uncertainty arises because the crystallized calcium silicate hydrates are found to have various chemical composition depending on the source of the data. Table 9 shows the composition considered in the EQ3/6 database and, for comparison, the composition represented in earlier work (see, e.g., Meike et al., 1994). Some of the differences are simply in the number of unit cells represented in a formula unit. In other cases, the difference rests in the amount of water or hydroxide in a formula unit. Such a difference is easy to understand in light of the fact that many of the hydrated phases are very sensitive to relative humidity and that the water content of these phases when measured may not have been controlled, and certainly has not been standardized (see, e.g., Bruton et al., 1994).

The last difference is more fundamental, and that is in the Ca:Si ratio of the formula unit. These differences reflect the poor state of knowledge of some of these phases at the structural level. A second potential uncertainty in thermodynamic values arises in that substitution of elements can occur, especially in natural samples. Thus, Al can substitute for some Si sites in a crystalline structure with consequent changes to the thermodynamic values measured. Such variabilities only contribute to uncertainty when the samples are not characterized with respect to these factors.

Table 9. Composition of C–S–H phases considered in the COM data file and in the cement project

Mineral	Comp. for Thermodynamic Data	Source	Comp. in the Cement Project
Afwillite	$Ca_3Si_2O_4(OH)_6$ or **$Ca_3Si_2H_6O_{10}$**	Jennings (1986)	$Ca_3Si_2O_4(OH)_6$ or **$Ca_3Si_2H_6O_{10}$**
Foshagite	$Ca_4Si_3O_9(OH)_2$:5H_2O or **$Ca_4Si_3H_{12}O_{16}$**	Jennings (1986)	$Ca_4Si_3O_9(OH)_2$ or **$Ca_4Si_3H_2O_{11}$**
Gyrolite	$Ca_2Si_3O_7(OH)_2$:1.5H_2O or **$Ca_4Si_6H_{10}O_{21}$**	Sarker and Barnes (1982) Barin et al. (1977)	$Ca_4Si_6O_{15}(OH)_2$:4H_2O or **$Ca_4Si_6H_{10}O_{21}$**
Hillebrandite	$Ca_2SiO_3(OH)_2$:0.17H_2O or **$Ca_2SiH_{2.34}O_{5.17}$**	Jennings (1986)	$Ca_2SiO_3(OH)_2$ or **$Ca_2SiH_2O_5$**
Jennite	–	–	$Ca_9Si_6O_{16}(OH)_2$:6H_2O or **$Ca_9Si_6H_{14}O_{24}$**
Nekoite	–	–	$Ca_3Si_6O_{12}(OH)_6$:5H_2O or **$Ca_3Si_6H_{16}O_{23}$**
Okenite	$CaSi_2O_4(OH)_2$:H_2O or **$Ca_{10}Si_{20}H_{40}O_{70}$**	Idealized	$Ca_{10}Si_{18}O_{46}$:18H_2O or **$Ca_{10}Si_{18}H_{36}O_{64}$**
Reyerite	–		$(Na,K)_2Ca_{14}(Si,Al)_{24}O_{58}(OH)_8$:6$H_2O$
Tobermorite-9Å	– **$Ca_5Si_6H_6O_{20}$**	Idealized	$Ca_5Si_6O_{16}(OH)_2$ or **$Ca_5Si_6H_2O_{18}$**
Tobermorite-11Å	– **$Ca_5Si_6H_{11}O_{22.5}$**	Idealized	$Ca_5Si_6O_{16}(OH)_2$:4H_2O or **$Ca_5Si_6H_{10}O_{22}$**
Tobermorite-14Å	– **$Ca_5Si_6H_{21}O_{27.5}$**		$Ca_5Si_6O_{16}(OH)_2$:8H_2O or **$Ca_5Si_6H_{18}O_{26}$**
Truscottite	– –		$Ca_{14}Si_{24}O_{58}(OH)_8$:2$H_2O$ or **$Ca_{14}Si_{24}H_{24}O_{68}$**
Xonotlite	$Ca_6Si_6O_{17}(OH)_2$ or **$Ca_6Si_6H_2O_{19}$**		$Ca_6Si_6O_{17}(OH)_2$ or **$Ca_6Si_6H_2O_{19}$**

6. Creation of the CEM.R27 Database

Our goal to develop a thermodynamic database that would allow us to simulate OPC degradation, both in systems that contain only cement and water and in those larger systems that include OPC cement or concrete at 25°C and at elevated temperatures, must be reached by a multi-step process. Our wish would be to develop the database from a foundation that has the highest degree of internal consistency. This would allow us to determine inconsistencies in the C–S–H phase data with the greatest degree of certainty. The obvious choice would seem to be the SUP data file. However, because of the manner in which that database is constructed and the limitations of the JEWEL program at the time we conducted this work, this was not possible for our purposes. A less efficient option, but one that better served our needs, was to remove chemical elements and related species from the COM data file that were not present in the SUP data file. At the time, it was impossible to suppress selected minerals or species from the COM data file unless they all belonged to a well-defined family of crystalline phases, such as the zeolites or carbonates, which is far too global for our needs.

Our solution was to remove the species manually from the COM data file, with the exception of certain aqueous species that are required to describe the solution composition most adequately. Next, all the minerals not present in the SUP data file were removed, with the exception of the cement-related minerals. These core data represented the heart of the new CEM.R27 database. Although not identical in structure, the new proto-database, which we refer to as SUP*, is identical in content to the database that would have been constructed from the real SUP file. The proto-database is first checked to determine whether the available chemical species in SUP are adequate, by running a comparison simulation of the same reactant file against each of the two databases, SUP and COM, and comparing the results. As a consequence, new aqueous species were added. Data corresponding to new minerals were subsequently added one at a time. The resultant growing database was tested incrementally, by simulating step-by-step, experimental results corresponding to equilibrium in the appropriate chemical system. The discussion below explains these steps in detail.

6.1 Selection of Aqueous Species for CEM.R27

The first database to be constructed will allow us to examine the Al–Ca–Cl–Fe–C–K–Mg–Na–S–Si chemical system. The chemical elements and aqueous species of interest for cement systems studies and present in the SUP data file are listed in the Table 10. For comparison, we list in Table 11 the set of aqueous species considered by Atkins et al. (1992) in the latest revision of their CEMENT database. One important distinction between the Atkins et al. (1992) CEMENT database and our CEM.R27 database is that we will include inorganic carbon species in our system. CO_2 and the aqueous carbonate species are of major importance in the cement systems for several reasons. First, by lowering the pH, aqueous carbonate species can lead to the dissolution of major phases, like the portlandite, impact the solid solution composition of phases such as the monosulphoaluminate and the calcium aluminate hydrates, and impact the Ca/Si ratio of amorphous-phase calcium silicate hydrates.

To measure the achievements of this study, we conducted a few preliminary calculations with both the SUP and COM data files and the database, using a typical OPC cement-phase reactant file (see Appendix B). The resultant calculated pore-water chemistries for typical cement pore solution compositions obtained with the SUP and the COM databases are shown in Table 12. Comparison of a typical composition of a pore solution in a mature paste, shown in Table 13 (data from Glasser and Marr, 1984, their Table 5), indicate that a good first-order approximation of the concentration of elements in solution could be achieved using either

database. The pH, ionic strength, and very high electrical imbalance of these initial simulations, although not listed here, reflected somewhat the uncertainty in the carbonate speciation and concentration in the experimental example. More importantly at this point, the simulations using the two databases disagree on the aqueous species distribution. The more correct distribution is not possible to verify with our experimental example, but it emphasizes the importance of including all relevant aqueous species in our new data file. Therefore, we returned the relevant aqueous species from the COM data file to the SUP* data file to provide a more complete and accurate description of the speciation of the aqueous phase.

Table 10. Aqueous species considered in the initial SUP database construction
Species present in duplicate are underlined.

Misc.	Al	Ca	Cl	Fe	C	K	Mg	Na	S	Si
H^+	Al^{+3}	Ca^{+2}	Cl^-	Fe^{+2}	HCO_3^-	K^+	Mg^{+2}	Na^+	HS^-	$SiO_{2(aq)}$
$O_{2(g)}$	$\underline{Al(CH_3COO)_2^+}$	$\underline{Ca(CH_3COO)_{2(aq)}}$	ClO^-	Fe^{+3}	$CO_{2(aq)}$	$KCl_{(aq)}$	$Mg(CH_3COO)_{2(aq)}$	$NaAlO_{2(aq)}$	S_2^{-2}	$HSiO_3^-$
$H_{2(aq)}$	$AlCH_3COO^{+2}$	$CaCO_{3(aq)}$	ClO_2^-		$Al(CH_3COO)_2^+$	$\underline{KHSO_{4(aq)}}$	$MgCO_{3(aq)}$	$Na(CH_3COO)_2^-$	$S_2O_6^{-2}$	$\underline{NaHSiO_{3(aq)}}$
$O_{2(aq)}$	$AlOH^{+2}$	$CaCl_{2(aq)}$	ClO_4^-		$AlCH_3COO^{+2}$	$\underline{KSO_4^-}$	$MgCH_3COO^+$	$NaCl_{(aq)}$	S_3^{-2}	
HO_2^-	$Al(OH)_2^+$	$CaHCO_3^{3+}$	$CaCl_{2(aq)}$		$Ca(CH_3COO)_{2(aq)}$		$MgCl^+$	$NaHSiO_{3(aq)}$	S_4^{-2}	
OH^-	AlO_2^-	$CaCH_3COO^+$	$KCl_{(aq)}$		$CaCO_{3(aq)}$		$MgHCO_3^+$	$NaOH_{(aq)}$	S_5^{-2}	
	$HAlO_{2(aq)}$	$CaCl^+$	$CaCl^+$		$CaHCO_3^+$				SO_3^{-2}	
		$CaSO_{4(aq)}$	$MgCl^+$		$CO_{(aq)}$				SO_4^{-2}	
			$NaCl_{(aq)}$		CO_2^{-2}				$S_2O_3^{-2}$	
					$CaCH_3COO^+$				$S_2O_4^{-2}$	
					$K(CH_3COO)_2^-$				$S_2O_3^{-2}$	
					$KCH_3COO_{(aq)}$				$S_3O_6^{-2}$	
					$\underline{Mg(CH_3COO)_{2(aq)}}$				$S_4O_6^{-2}$	
					$\underline{MgCO_{3(aq)}}$				$S_5O_6^{-2}$	
					$\underline{MgCH_3COO^+}$				$CaSO_{4(aq)}$	
					$MgHCO_3^+$				$H_2S_{(aq)}$	
									HSO_4^-	
									$KHSO_{4(aq)}$	
									$SO_{2(aq)}$	
									KSO_4^-	
									$S_2O_5^-$	

Table 11. **Aqueous species considered by Atkins et al. (1992) in their cement data file**
Species present in duplicate are underlined.

Misc.	Al	Ca	K	Mg	Na	S	Si
H^+	Al^{+3}	Ca^{+2}	K^+	Mg^{+2}	Na^+	SO_4^{-2}	H_4SiO_4
H_2O	$AlOH^{+3}$	$CaOH^+$	KOH	$MgOH^+$	$NaOH$	HSO_4^-	$H_3SiO_4^-$
OH^-	$Al(OH)_2^+$	$\underline{CaSO_4}$	$\underline{KSO_4^-}$	$Mg_4(OH)_4^{+4}$	$\underline{NaSO_4^-}$	S^{-2}	$H_2SiO_4^{-2}$
	$Al(OH)_3$	$\underline{CaH_2SiO_4}$		$\underline{MgSO_4}$	$\underline{Na_2SO_4}$	HS^-	CaH_2SiO_4
	$Al(OH)_4^-$	$\underline{CaH_3SiO_4^+}$		$\underline{Mg(H_2SiO_4^-)}$		H_2S	$CaH_3SiO_4^+$
	$Al_2(OH)_2^{+4}$	$\underline{Ca(H_3SiO_4)_2}$		$\underline{Mg(H_3SiO_4)^+}$		$CaSO_4$	$Ca(H_3SiO_4)_2$
	$Al_3(OH)_4^{+5}$			$\underline{Mg(H_3SiO_4)_2}$		KSO_4^-	$Mg(H_2SiO_4)$
	$\underline{AlSO_4^+}$					$NaSO_4^-$	$Mg(H_3SiO_4)^+$
	$\underline{Al(SO_4)_2^-}$					Na_2SO_4	$Mg(H_3SiO_4)_2$
	$\underline{AlHSO_4^{+2}}$					$AlSO_4^+$	
						$Al(SO_4)_2^-$	
						$AlHSO_4^{+2}$	
						$MgSO_4$	
						H_2SO_4	

Table 12. **Comparison of aqueous species distribution in a typical cement pore solution**
at 25°C
Atkins et al. (1992) species are in bold.

		EQ3NR Calculations			
		COM Data File		SUP Data File	
Element	Aqueous Species	Molality	Percent	Molality	Percent
Al	**Al(OH)$_4^-$**	8.70×10^{-5}	100	—	—
	Al(OH)$_{3(aq)}$	4.36×10^{-12}	5.00×10^{-6}	—	—
	Al(OH)$_2^+$	4.80×10^{-19}	5.52×10^{-13}	—	—
	Al(OH)$^+$	1.06×10^{-26}	1.22×10^{-20}	—	—
	Al^{+3}	1.66×10^{-4}	—	—	—
	AlO$_2^-$ ($\Leftrightarrow$Al(OH)$_4^-$)	—	—	8.66×10^{-5}	99.55
	NaAlO$_{2(aq)}$	—	—	3.90×10^{-7}	0.45
Ca	**Ca^{+2}**	1.02×10^{-3}	49.71	2.04×10^{-3}	98.78
	CaOH$^+$	9.34×10^{-4}	45.32	—	—
	CaH$_2$SiO$_{4(aq)}$	8.66×10^{-5}	4.20	—	—
	CaSO$_{4(aq)}$	8.83×10^{-6}	4.28×10^{-1}	1.80×10^{-5}	0.88
	CaCO$_{3(aq)}$	7.03×10^{-6}	3.41×10^{-1}	7.03×10^{-6}	0.34
	CaH$_3$SiO$_4^+$	8.60×10^{-10}	4.17×10^{-5}	—	—
	CaHCO$_3^+$	7.51×10^{-11}	3.64×10^{-6}	7.53×10^{-11}	3.66×10^{-6}
	Ca(H$_3$SiO$_4$)2$_{(aq)}$	3.94×10^{-13}	1.92×10^{-8}	—	—
C	CO$_3^{-2}$	3.25×10^{-5}	79.28	1.66×10^{-5}	70.20
	CaCO$_{3(aq)}$	7.03×10^{-6y}	17.18	7.04×10^{-6}	29.74
	NaCO$_3^-$	1.43×10^{-6}	3.48	—	—
	HCO$_3^-$	1.99×10^{-8}	0.05	1.01×10^{-8}	0.05
	MgCO$_{3(aq)}$	4.88×10^{-9}	0.01	5.42×10^{-9}	0.03

Element	Aqueous Species	EQ3NR Calculations			
		COM Data File		SUP Data File	
		Molality	Percent	Molality	Percent
	$NaHCO_{3(aq)}$	6.75×10^{-10}	< 0.01	—	—
	$CaHCO_3^+$	7.51×10^{-11}	< 0.01	7.53×10^{-11}	< 0.01
	$MgHCO_3^+$	1.13×10^{-13}	< 0.01	1.27×10^{-13}	< 0.01
	$CO_{2(aq)}$	2.15×10^{-15}	< 0.01	1.09×10^{-15}	< 0.01
K	**K^+**	1.50×10^{-1}	96.50	1.55×10^{-1}	99.85
	$KOH_{(aq)}$	5.22×10^{-3}	3.36	—	—
	KSO_4^-	2.21×10^{-4}	0.14	2.37×10^{-4}	0.15
Mg	**$MgH_2SiO_{4(aq)}$**	1.61×10^{-6}	53.62	—	—
	Mg^{+2}	1.36×10^{-6}	45.30	2.99×10^{-6}	99.82
	$MgSO_{4(aq)}$	2.73×10^{-8}	0.91	—	—
	$MgCO_{3(aq)}$	4.88×10^{-9}	0.17	5.42×10^{-9}	0.18
Na	**Na^+**	4.46×10^{-2}	93.39	4.69×10^{-2}	98.22
	$NaOH_{(aq)}$	3.10×10^{-3}	6.49	7.81×10^{-4}	1.63
	$NaSO_4^-$	5.94×10^{-5}	0.12	—	—
	$NaCO_3^-$	1.42×10^{-6}	< 0.01	—	—
	$NaHSiO_{3(aq)}$	—	—	6.89×10^{-5}	0.15
S	**SO_4^{-2}**	7.51×10^{-4}	72.15	7.85×10^{-4}	75.49
	KSO_4^-	2.21×10^{-4}	21.28	2.37×10^{-4}	22.78
	$NaSO_4^-$	5.94×10^{-5}	5.72	—	—
	$CaSO_{4(aq)}$	8.83×10^{-6}	0.85	1.81×10^{-5}	1.73
Si	**$CaH_2SiO_{4(aq)}$**	8.66×10^{-5}	66.08	—	—
	$H_2SiO_4^{-2}$	4.25×10^{-5}	32.41	—	—
	$MgH_2SiO_{4(aq)}$	1.61×10^{-6}	1.23	—	—
	$NaHSiO_{3(aq))}$	1.87×10^{-7}	0.14	6.89×10^{-5}	52.59
	$HSiO_3^-$	1.77×10^{-7}	0.14	6.21×10^{-5}	47.39
	$SiO_{2(aq)}$	—	—	2.85×10^{-8}	0.02

Table 13. Composition of pore solution in a mature paste (after Glasser and Marr, 1984, Table 5)

Element	Composition (mmol/L)
$SiO_{2(aq)}$	0.131
Ca^{+2}	2.06
Na^+	47.8
K^+	155.4
Al^{+3}	0.087
SO_4^{-2}	1.04
Mg^{+2}	0.003
pH	13.17

6.2 Addition of Data for Mineral Phases

The next step in development of the CEM data file is to assess the thermodynamic data already available in the GEMBOCHS database for the phases that might be formed in room-temperature and thermally treated cement. These phases in the chemical systems, which we discuss below, can form even over long time periods at temperatures between 25° and 250°C. Subsequently, we will calculate the solubility products for phases not already represented in the database. We examine the phases system by system with increasing complexity. The five chemical systems, as follows, are discussed:

- $CaO–SiO_2–H_2O$
- $CaO–Al_2O_3–H_2O$
- $CaO–Al_2O_3–SO_3–H_2O$
- $CaO–Al_2O_3–CO_2–H_2O$
- $CaO–Al_2O_3–SiO_2–SO_3–H_2O$

6.2.1 CaO–SiO$_2$–H$_2$O System

The phases present in this system are $Ca(OH)_2$ and calcium silicate hydrate. Depending on temperature and other parameters, such as curing condition, maturity of the paste, and correlative humidity, the calcium silicate hydrate phases can be in an amorphous or nearly amorphous state (at room temperature) or in a semi-crystalline or crystalline state (at elevated temperatures and over time).

Solubility Product for Ca(OH)$_2$. The COM data file initially contains data for the portlandite phase, as shown Table 14. The thermodynamic data used for the extrapolation algorithm come from Robie et al. (1979).

Table 14.   Thermodynamic data for portlandite given in the COM data file

```
Portlandite        Ca(OH)2
    sp.type = solid
*   EQ3/6 = com, alt, pit
    revised = 17-may-1990
*   mol.wt. = 74.093 g/mol
    V0PrTr = 33.056 cm**3/mol [source:     ]
****
    3 element(s):
    1.0000 Ca    2.0000 H          2.0000 O
****
    4 species in aqueous dissociation reaction:
    −1.0000 Portlandite    −2.0000 H+
    1.0000 Ca++          2.0000 H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
    24.6242  22.5552  20.1960  18.0608
    15.9702  14.3128  12.9403  11.7465
*
*   gflag = 1 [reported delG0f]
*   extrapolation algorithm: Cp integration
*   ref-state data [source: 79rob/hem]
*       delG0f = −898.408 kj/mol   [reported]
*       delH0f = −986.070 kj/mol   [reported]
*       S0PrTr = 83.390 j/(mol*K)  [reported]
*   Cp coefficients [source: 79rob/hem units: jou]
*       T**0 = 0.18667000E+03
*       T**1 =−0.21911000E−01
*       T**−.5 =−0.15998000E+04
*       Tlimit = 426.85C
```

A simple EQ3NR calculation with these data yields the following composition for the solution in equilibrium with portlandite: [Ca] = 15.7 mmol/L, and pH = 12.4. The calculated values are different from the compositions usually observed for this mineral: average value of [Ca] = 20–22 mmol/L (see Duchesne and Reardon, 1995, their Table 2). According to the observations made by Duchesne and Reardon, the finer the crystal morphology of Ca(OH)$_2$, the greater the solubility product. In a cement, the crystals of portlandite are more likely to precipitate as small crystals. The consequent high surface energy probably contributes to the free energy of formation. This suggests that the solubility product of portlandite could be corrected to give a more accurate description of the Ca(OH)$_2$ morphology in cement.

A new value of the solubility product has been calculated from solubility measurements conducted by Duchesne and Reardon and from data collected from the literature (log K_{sp} = 22.8622 at 25°C). A test with this new value leads to a more satisfying composition for the solution in equilibrium with portlandite: [Ca] = 21.1 mmol/L, and pH = 12.5. Therefore, the Duchesne and Reardon value was introduced into the CEM database.

Estimation of Solubility Products for Amorphous C–S–H Phases. At the time this work was conducted, the GEMBOCHS database contained no data related to amorphous calcium silicate hydrates. Certain authors (Fujii and Kondo, 1983; Glasser et al., 1987a; Gartner and Jennings, 1987; and Berner, 1990) have developed thermodynamic and chemical models to calculate the solubility product of the amorphous C–S–H gel as a function of its composition (Ca/Si ratio in general; see the discussion above). Considering the structure as well as the primary goal of our database development, which is to study higher-temperature cases, only data corresponding to discrete compositions of the gel were entered into the data file. These discrete compositions serve to represent the whole range of compositions generally observed in cement pastes. Solubility data for three compositions (Ca/Si = 0.9, 1.3, and 1.7) have been determined experimentally by Atkins et al. (1991, 1992). The solubility product calculations are shown in Table 15.

**Table 15.   Calculation of solubility products of C–S–H gels
After solubility measurement data obtained by Atkins et al. (1991, 1992)**

Ca/Si	Days	Aqueous Characterization (mmol/dm³)			Solid Characterization	Calculated Activities (EQ3NR)			Elec. Imb.	Log K_{sp}
		[Ca]	[SiO$_2$]	[OH$^-$]	(XRD)	(Ca^{+2})	(SiO$_2$)	(H$^+$)	(%)	(25°C)
0.9	35	1.06	0.124	1.1	C–S–H	−3.08	−5.03	−11.01	2.0	12.02
	70	1.77	0.130	3.1	C–S–H	−2.89	−2.45	−11.46	3.6	12.56
	100	1.56	0.140	3.05	C–S–H	−2.95	−5.41	−11.45	−2.2	12.55
1.3	35	9.67	<0.01	19.3	C–S–H	−2.34	−7.53	−12.21	−3.2	21.20
	70	12.0	0.007	21.5	C–S–H	−2.26	−7.64	−12.26	1.8	21.28
	100	7.49	0.017	14.6	C–S–H + C $\overline{C}$	−2.41	−7.05	−12.10	−1.6	21.27
1.7	35	15.75	<0.01	29.6	C–S–H + CH + C $\overline{C}$	−2.19	−7.67	−12.39	−1.8	30.73
	70	20.41	0.004	41.5	C–S–H + CH + C $\overline{C}$	−2.13	−8.25	−12.52	−5.8	30.69
	100	20.27	<0.01	39.5	C–S–H + C $\overline{C}$	−2.13	−8.13	−12.50	−3.2	30.75

More recent work (Damidot et al., 1994) takes into account only two different compositions of C–S–H: a C–S–H(SI) and a C–S–H(SII). The first phase has a low Ca/Si ratio (about 1.1) and is formed for calcium concentrations less than 20 mmol/L. The second phase is formed at a higher Ca/Si ratio and has an average Ca/Si ratio of 1.8. Experiments were carried out by these authors to measure the solubility of the two phases. EQ3NR calculations conducted with these analytical values led to the results shown in Table 16. The new values

agree well with the values calculated in Table 15, as shown in Figure 2, giving the evolution of the calculated solubility product versus the Ca/Si ratio of the C–S–H gel.

Table 16. **Calculation of solubility products of C–S–H gels after solubility measurement**
Data obtained by Damidot et al. (1994).

	Aqueous Characterization (mmol/kg)			Calculated Activities (EQ3NR)			Log K_{sp}
Ca/Si	[Ca]	(SiO$_2$)	[OH$^-$]	(Ca^{+2})	(SiO$_2$)	(H$^+$)	(25°C)
1.1	1.228	1.116	11.03	−3.03	−4.17	−11.11	16.93
1.8	5.212	2.895	11.69	−2.56	−4.47	−11.79	33.44
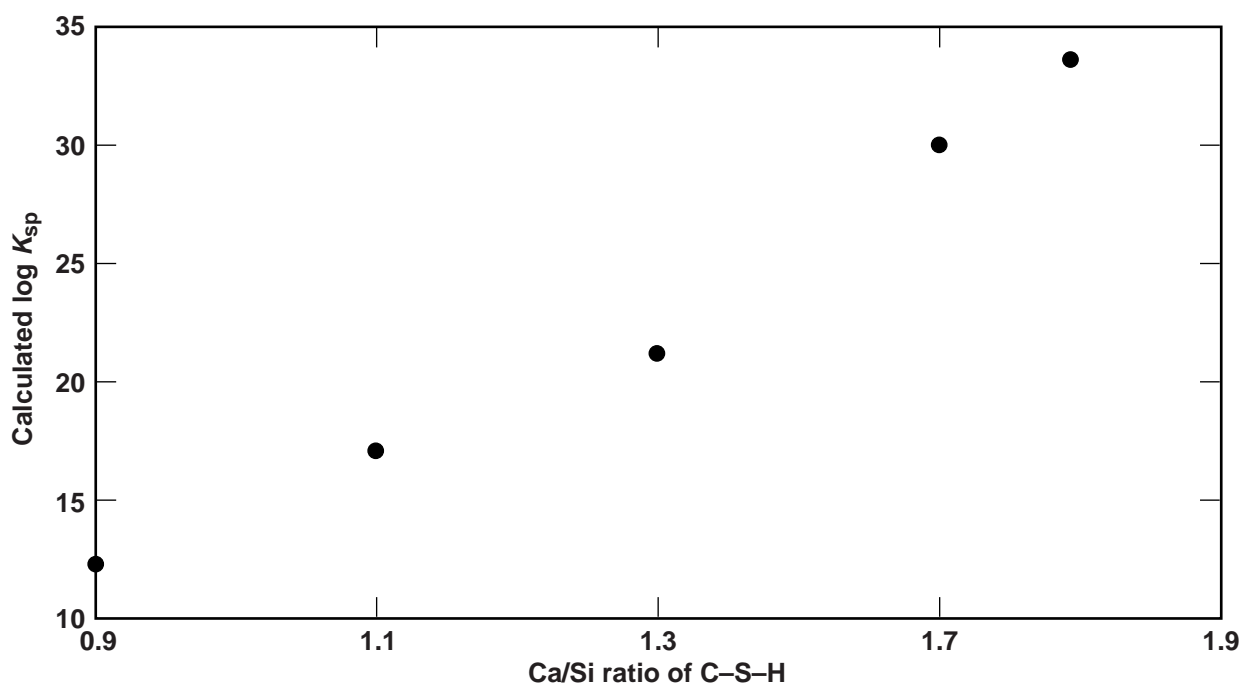
Figure 2. **Evolution of the solubility product versus Ca/Si ratio of C–S–H**

Of the five reference data that are available for Ca/Si ratio between 0.9 and 1.8, three have been added as of this report to the CEM data file, corresponding to the following Ca/Si ratios: 0.9, 1.3, and 1.7. The N–C–S–H and K–C–S–H systems have not been considered in this version of the database.

Solubility Products for Crystalline Calcium Silicate Hydrates. At the time of this report, the data available in GEMBOCHS for the crystalline calcium silicate hydrates are as listed in Table 7 and Table 8. With the exception of the data for tobermorite-9Å, all the thermodynamic data originate from Sarker et al. (1982). They can be traced to Babushkin et al. (1985), which can, in turn, be traced to older references of the same authors. These data were not determined experimentally in most cases, but were arrived at by estimation methods. The lack of thermodynamic constants for structurally similar phases, some lack of internal consistency in the values reported, and uncertainty in the methods that were used for estimation necessitate that the values be verified. Other than these references, the literature is

not rich in thermodynamic constants for the crystalline C–S–H phases. The value originally present in the GEMBOCHS database for tobermorite-9Å is 69.08. Attempts to determine the solubility product of tobermorite-9Å undertaken by Atkins et al. (1992) demonstrate the various problems encountered with many of the phases, among which are carbonation, incongruent dissolution, and evolution of the measurements with time (supposedly due to evolving degree of the crystallinity). However, assuming the congruency for the dissolution reaction in Eq. (1), they determined a value for the solubility product of 65.05.

$$C_5S_6H_5 + 2\ H_2O + 10\ H^+ \rightarrow 5\ Ca^{+2} + 6\ H_4SiO_4 \ . \tag{1}$$

Using the average results given by these authors for the composition of the solution in equilibrium with tobermorite-9Å, a solubility product is calculated (Table 17) for the following dissolution reaction:

$$C_5S_6H_5 + 10\ H^+ \rightarrow 5\ Ca^{+2} + 6\ SiO_{2(aq)} + 8\ H_2O \ . \tag{2}$$
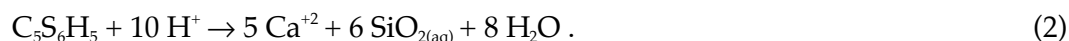
Table 17.   Estimation of a solubility product for tobermorite-9Å
After analytical data of Atkins et al. (1992, their Table 4.9, p. 29)

Analysis	Balance Calculation Option	Aqueous Characterization (mmol/dm³)			Solid Characterization (XRD)	Calculated Activities (EQ3NR)			Elec. Imb. (%)	Log K_{Sp} (25°C)
		[Ca]	[SiO₂]	[OH⁻]		(Ca⁺²)	(SiO₂)	(H⁺)		
1	none	0.62	0.63	1.15	Tobermorite +	−3.30	−4.34	−11.03	−16.8	67.76
	H⁺				trace of calcite	−3.29	−4.13	−10.80	—	66.77
2	none	0.34	0.26	0.65	Tobermorite +	−3.54	−4.51	−10.80	−13.7	63.24
	H⁺				trace of calcite	−3.53	−4.37	−10.64	—	62.53
3	none	0.30	0.25	0.40	Tobermorite +	−3.58	−4.33	−10.58	0.31	61.92
	H⁺				trace of calcite	−3.58	−4.33	−10.57	—	61.82

We assumed an increasing degree of carbonation during the experiments and, therefore, introduced only the first value of 66.77 into the CEM data file. Further studies conducted by the same authors, which examine the Al-bearing tobermorite, have not been included in this version of the CEM database.

6.2.2 CaO–Al₂O₃–H₂O System

Calculation of the Solubility Product for C₃AH₆. Most of the thermodynamic data for this phase have been recently determined by Atkins et al. (1991, 1992) from direct synthesis and multiple filtration/redispersion procedures (Table 18). Data obtained by D'Ans and Eick (1953) are also available. Calculations of the speciation of aqueous species have been conducted with EQ3NR from both sets, indicating rather high electrical imbalance in most of the analytical results. The solubility product was calculated using the reaction

$$C_3AH_6 + 12\ H^+ \rightarrow 3\ Ca^{+2} + 2\ Al^{+3} + 12\ H_2O \ . \tag{3}$$
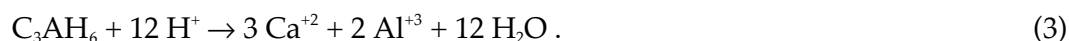
Table 18. Estimation of a solubility product for C_3AH_6
After analytical data of Atkins et al. (1992, Tables 4.1 and 4.2, pp. 20 and 21)

Source	Analysis	Aqueous Characterization (mmol/dm³)			Solid Characterization (XRD)	Balance Calculation Option	Calculated Activities (EQ3NR)			Elec. Imb. (%)	Log K_{sp} (25°C)
		[Ca]	[Al]	[OH⁻]			(Ca⁺²)	(Al⁺³)	(H⁺)		
Atkins et al. (1992)	1	7.43	4.40	23.4		none	−2.39	−28.72	−12.29	−30.4	82.87
						H⁺	−2.39	−27.25	−11.93		81.49
	2	7.31	4.81	27.0		none	−2.41	−28.93	−12.36	−37.1	82.23
						H⁺	−2.40	−27.10	−11.90		81.40
	3	5.11	5.20	23.3	C_3AH_6	none	−2.34	−28.65	−12.30	−47.2	83.28
						H⁺	−2.52	−25.95	−11.62		79.98
	4	5.16	3.80	23.4		none	−2.54	−28.80	−12.30	−45.0	82.38
						H⁺	−2.52	−26.54	−11.73		80.12
	5	6.49	4.80	29.6		none	−2.46	−29.08	−12.40	−45.2	83.38
						H⁺	−2.44	−26.80	−11.83		81.04
	6	5.33	4.40	28.1		none	−2.53	−29.04	−12.38	−50.6	83.01
						H⁺	−2.50	−26.40	−11.72		80.34
D'Ans and Eick (1953)	1	3.33	2.22	13.3	C_3AH_6 in water	none	−2.68	−28.09	−12.07	−40.0	80.62
						H⁺	−2.67	−26.16	−11.59		78.75
	2	3.56	1.28	11.0	C_3AH_6 in undersaturated CH solutions	none	−2.64	−28.02	−11.98	−27.0	79.80
						H⁺	−2.65	−26.86	−11.70		78.73
	3	7.55	0.20	15.7		none	−2.37	−29.39	−12.13	−2.53	79.67
						H⁺	−2.40	−29.21	−12.08		79.34
	3a	20.93	0.064	42.1	C_3AH_6 in saturated CH solutions	none	−2.03	−31.50	−12.53	−0.41	81.27
						H⁺	−2.11	−31.32	−12.48		80.79

Atkins et al. (1992) explain the small variations in component concentrations in terms of measurement errors. However, calculations of the speciation from these measurements indicate strong electrical imbalances between 30 and 50%, as shown in Table 18. A second series of calculations has been done using a correction on the pH value to ensure neutrality of the solution. These results are shown in Table 18 as well. Tests with a correction of the Al concentrations were also done. However, the magnitude of the corrections were in every case too important for the calculations to be undertaken with EQ3NR.

The same type of calculations were done from the data of D'Ans and Eick (1953). The experiments carried out by these authors were done with C_3AH_6 in water for Sample 1 and C_3AH_6 in undersaturated and saturated CH solutions for the other samples. Atkins et al. explained the discrepancies with their own results by the short duration of the D'Ans and Eick experiments: equilibration would not have been completed.

A value of 80.73 is retained for the CEM data file, corresponding to the average value calculated from the Atkins et al. experimental results, the electrical imbalance being corrected by the pH. As will be shown later, this value will be tested and, if necessary, adjusted with compatibility experiments.

Estimation of the Solubility Product for C_4AH_{13}. Thermodynamically, C_3AH_6 is favored over C_4AH_{13} at room temperature. However, because its presence is almost always observed in regular cement systems, it is an important phase to characterize for young cements. An added consequence of the metastability is that C_4AH_{13} has not been synthesized as a pure phase. Therefore, solubility experiments contain impurities that affect the aqueous phase composition and ultimately the value of the solubility product. With time, however, CH and

C_3AH_6 become dominant after dispersions and aging, controlling the solubilities of Ca and OH. Therefore, for the Yucca Mountain Project, uncertainty in this value is less significant.

The solubility product was calculated using the reaction

$$C_4AH_{13} + 14\,H^+ \rightarrow 4\,Ca^{+2} + 2\,Al^{+3} + 20\,H_2O \,. \tag{4}$$
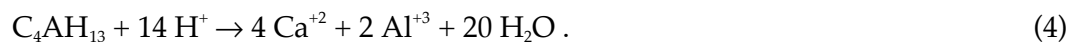
As already observed for C_3AH_6, the EQ3NR speciations present electrical imbalances. These imbalances were corrected by adjusting the pH, as shown in Table 19. An average value of 103.33 was introduced to the CEM data file. It is interesting to note that the phase assemblages observed experimentally for the eight assemblages are also predicted through the EQ3NR calculations with the CEM data file.

Table 19. **Estimation of a solubility product for C_4AH_{13}**
After analytical data of Atkins et al. (1992, their Table 4.4, p. 23); the solids characterized are listed in order of decreasing importance.

Analysis	Aqueous Characterization (mmol/dm³)			Solid Characterization (XRD)	Balance Calculation Option	Calculated Activities (EQ3NR)			Elec. Imb. (%)	Log K_{sp} (25°C)
	[Ca]	[Al]	[OH⁻]			(Ca^{+2})	(Al^{+3})	(H^+)		
1	20.47	0.07	—	C_4AH_{13}, CH, C_3AH_6	none	−2.13	−31.47	−12.53	7.00	103.94
					H⁺	−2.12	−31.25	−12.47		103.60
2	19.11	0.09	38.1	C_4AH_{13}, CH, C_3AH_6	none	−2.14	−31.20	−12.49	−5.31	103.85
					H⁺	−2.14	−31.03	−12.45		103.68
3	20.11	0.05	40.0	C_4AH_{13}, CH, C_3AH_6	none	−2.13	−31.54	−12.51	−5.33	103.52
					H⁺	−2.12	−31.37	−12.47		103.36
4	19.76	0.04	40.9	C_4AH_{13}, CH, C_3AH_6	none	−2.14	−31.68	−12.52	−7.42	103.35
					H⁺	−2.13	−31.44	−12.46		103.04
5	18.71	0.07	37.5	C_4AH_{13}, CH, C_3AH_6	none	−2.15	−31.29	−12.48	−5.52	103.59
					H⁺	−2.14	−31.11	−12.44		103.38
6	17.74	<0.05	37.7	C_4AH_{13}, C_3AH_6, CH?	none	−2.17	−31.44	−12.49	−8.42	103.23
					H⁺	−2.16	−31.11	−12.42		102.70
7	17.53	0.06	36.8	C_4AH_{13}, C_3AH_6, CH?	none	−2.18	−31.33	−12.48	−7.74	103.32
					H⁺	−2.16	−31.27	−12.42		103.08
8	15.34	0.27	31.25	C_3AH_6, C_4AH_{13}	none	−2.21	−30.40	−12.41	−6.04	104.11
					H⁺	−2.20	−30.20	−12.36		103.84

6.2.3 CaO–Al₂O₃–SO₃–H₂O System

Calculation of the Solubility Product for Ettringite. The more complete experimental dataset for the solubility of ettringite (AFt) at 25°C has been determined by Atkins et al. (1992) and more recently by Warren and Reardon (1994). In the Atkins et al. study, some of the charge imbalances are as high as 50%. The Warren and Reardon study provides solubility data from ettringite/water equilibration experiments conducted from both undersaturation and supersaturation and over a wide range of pH conditions (10.4 to 13.7). Warren and Reardon used different approaches to derive the ionic activity product of ettringite from their analytical data. For pH values lower than 12, they showed that the most accurate results were obtained when the model was allowed to calculate the sulfate concentration. For pH values greater than 12, the correction on the pH was found to be more adequate.

Keeping these observations in mind, we recalculated the ionic activity products of ettringite from both datasets using three options in EQ3NR: no correction of the imbalance,

correction with SO_4^{-2} concentration, and correction on the pH. The results are shown in Tables 20 to 24 (following pages).

The solubility product was calculated using the reaction

$$AFt + 12\,H^+ \rightarrow 6\,Ca^{+2} + 2\,Al^{+3} + 3\,SO_4^{-2} + 38\,H_2O \,. \tag{5}$$
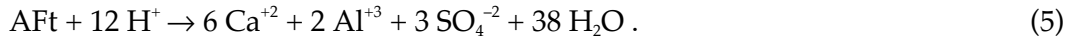
The curve plotting the evolution of the ionic activity product versus pH indicates the deviation already observed by Warren and Reardon for pH values higher than 13. According to Warren and Reardon, the deviation could be due to a progressive structural transformation, or it may be a reflection of systematic errors associated with the ionic activity coefficient model (the ionic strengths observed for these pH values are in the range 0.2 to 1.0, in which the reliability of the Debye–Hückel model is not really good).

The value of 58.0 inserted in the CEM data file corresponds to the average value in the plateau observed for pH values in the range of 10.5 to 12.5 (Figure 3). This value would be corrected later, when calculating the equilibrium composition of typical assemblages.
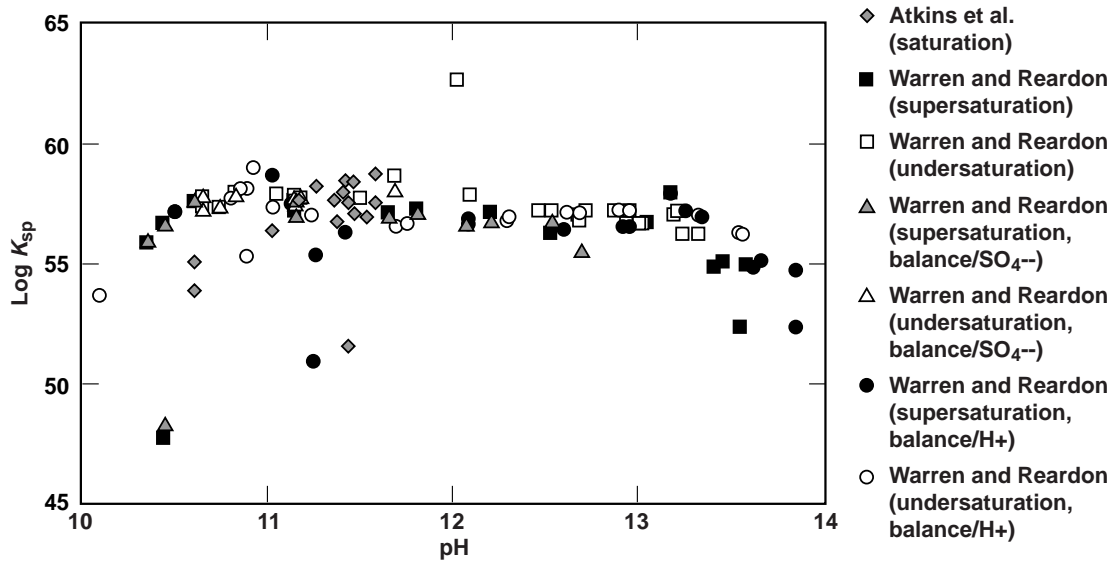
Figure 3. **Calculated log solubility product (log K_{sp}) for ettringite within the pH range of 10–14**

Estimation of a Solubility Product for Monosulfate. The monosulfate (AFm) is thermodynamically metastable relative to both AFt and C_3AH_6 in water at 25°C (Turriziani, 1964; Brown and Lacroix, 1989). However, its presence is commonly observed in cement systems over long periods of time.

The literature does not provide any thermodynamic data specific to the system AFm–H_2O. As for C_4AH_{13}, the calculations are severely complicated because this phase is difficult to isolate as a pure phase in water. Data relative to the composition of solutions in equilibrium with monosulfate were generated by Atkins et al. (1992) (see Table 25). These data show that the dissolution of AFm is incongruent (low concentration in SO_4, which disappears by precipitation of ettringite). The calculation of a simple solubility product is not valid from the thermodynamic point of view. However, a value is derived here from the analytical data, assuming congruency. The solubility product was calculated using the reaction

$$AFt + 12\,H^+ \rightarrow 6\,Ca^{+2} + 2\,Al^{+3} + 3\,SO_4^{-2} + 38\,H_2O \,. \tag{6}$$
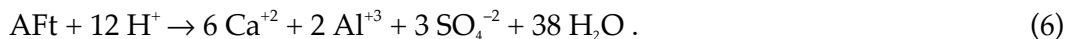
An average value of 72.60 was introduced in the CEM data file.

Table 20.   Estimation of a solubility product for ettringite (AFt) at 25°C
After analytical data of Atkins et al. (1992, their Table 4.5, p. 25); values in italic must be considered with caution.

Analysis	Aqueous Characterization (mmol/dm³)				Solid Characterization (XRD)	Balance Calculation Option	Calculated Activities (EQ3NR)				Elec. Imb. (%)	Log K_{sp} (25°C)
	$[Ca^{+2}]$	$[Al^{+3}]$	$[SO_4^{-2}]$	$[OH^-]$			(Ca^{+2})	(Al^{+3})	(SO_4^{-2})	(H^+)		
1	2.67	0.29	1.68	2.90		none	−2.78	−26.35	−3.01	−11.42	−11.0	58.41
						H^+	−2.89	−25.38	−3.00	−11.17		57.61
						SO_4^{-2}	−2.77	−26.37	−3.21	−11.42		58.04
2	2.00	0.41	1.20	2.60		none	−2.88	−26.03	−3.12	−11.37	−15.9	57.64
						H^+	−2.88	−24.64	−3.12	−11.03		56.39
						SO_4^{-2}	−2.86	−26.04	−3.53	−11.37		56.67
3	2.29	0.54	0.98	3.10	AFt	none	−2.82	−26.21	−3.22	−11.45	−10.5	58.29
						H^+	−2.73	−25.48	−3.22	−11.26		58.18
						SO_4^{-2}	−2.82	−26.22	−3.57	−11.45		57.37
4	1.82	0.65	1.27	4.20		none	−2.93	−26.65	−3.10	−11.58	−35.6	58.68
						H^+	−2.92	−22.76	−3.09	−10.61		54.99
						SO_4^{-2}						
5	1.43	0.41	1.00	4.20		none	−3.02	−26.86	−3.19	−11.58	−41.0	57.50
						H^+	−3.00	−22.98	−3.17	−10.61		53.85
						SO_4^{-2}						
6	1.25	0.41	1.00	3.70		none	−3.07	−26.65	−3.18	−11.53	−43.4	56.99
						H^+	*−3.05*	*−20.19*	*−3.16*	*−9.91*		*50.78*
						SO_4^{-2}						
7	1.21	0.59	1.04	3.30	AFt + traces $CaCO_3$	none	−3.10	−26.30	−3.16	−11.48	−43.9	57.09
						H^+	*−3.08*	*−5.57*	*−3.14*	*−6.28*		*36.39*
						SO_4^{-2}						
8	1.97	0.37	0.97	3.00		none	−2.88	−26.33	−3.22	−11.44	−15.6	57.60
						H^+	−3.89	−26.35	−3.21	−11.44		51.60
						SO_4^{-2}	−2.89	−26.35	−3.21	−11.44		57.60

Table 21. Estimation of a solubility product for ettringite (AFt) at 25°C
After analytical data of Warren and Reardon (1994) for supersaturation
conditions and for the first batch of experiments

Analysis	Aqueous Characterization (mmol/dm³)					Balance Calculation Option	Calculated Activities (EQ3NR)				Elec. Imb. (%)	Log K_{sp} (25°C)
	$[Ca^{+2}]$	$[Al^{+3}]$	$[SO_4^{-2}]$	$[Na^+]$	pH		(Ca^{+2})	(Al^{+3})	(SO_4^{-2})	(H^+)		
a1	6.31	0.05	7.85	4.47	10.36	none	−2.55	−22.90	−2.45	−10.36	3.81	55.84
						H^+	−2.56	−25.62	−2.45	−11.04		58.54
						SO_4^{-2}	−2.56	−22.90	−2.42	−10.36		55.87
b1	4.79	0.19	6.85	3.55	10.45	none	−2.65	−22.70	−2.48	−10.45	−4.69	56.63
						H^+	—	—	—	—		
						SO_4^{-2}	−2.64	−22.70	−2.51	−10.45		56.59
c1	1.51	0.49	5.13	7.50	11.15	none	−3.13	−25.08	−2.55	−11.45	−8.67	57.22
						H^+	—	—	—	—		
						SO_4^{-2}	−3.11	−25.08	−2.62	−11.45		57.11
d1	0.49	1.38	5.58	14.6	11.66	none	−3.65	−26.68	−2.53	−11.66	−7.11	57.06
						H^+	−3.65	−25.69	−2.52	−11.42		56.21
						SO_4^{-2}	−3.63	−26.67	−2.62	−11.66		56.92
e1	0.22	2.00	5.94	28.1	12.07	none	−4.05	−28.16	−2.56	−12.07	1.07	56.56
						H^+	−4.05	−28.24	−2.56	−12.09		56.64
						SO_4^{-2}	−4.05	−28.16	−2.54	−12.07		56.59
f1	0.13	2.50	6.21	65.9	12.53	none	−4.38	−29.92	−2.65	−12.53	7.11	56.25
						H^+	−4.40	−30.24	−2.66	−12.61		56.43
						SO_4^{-2}	−4.42	−29.92	−2.44	−12.53		56.68
g1	0.14	2.25	6.76	139	13.05	none	−4.59	−32.07	−2.78	−13.05	−9.18	56.25
						H^+	−4.55	−31.73	−2.76	−12.96		56.47
						SO_4^{-2}						
h1	0.19	2.49	7.49	273	13.22	none	−4.58	−32.72	−2.87	−13.22	4.13	57.11
						H^+	−4.60	−32.87	−2.87	−13.26		57.15
						SO_4^{-2}						
i1	0.13	0.84	13.1	737	13.47	none	−4.93	−34.21	−2.88	−13.47	22.0	55.01
						H^+	−5.06	−34.99	−2.90	−13.67		55.01
						SO_4^{-2}						
j1	0.08	1.06	42.5	1240	13.59	none	−5.25	−34.59	−2.52	−13.59	28.9	54.84
						H^+	−5.43	−35.68	−2.55	−13.86		54.61
						SO_4^{-2}						

Thermodynamics of Calcium Silicate Hydrates

Table 22. Estimation of a solubility product for ettringite (AFt) at 25°C
After analytical data of Warren and Reardon (1994) for supersaturation
conditions and for the second batch of experiments

Analysis	Aqueous Characterization (mmol/dm³)					Balance Calculation Option	Calculated Activities (EQ3NR)				Elec. Imb. (%)	Log K_{sp} (25°C)
	[Ca^{+2}]	[Al^{+3}]	[SO$_4^{-2}$]	[Na$^+$]	pH		(Ca^{+2})	(Al^{+3})	(SO$_4^{-2}$)	(H$^+$)		
a2	0.82	0.004	0.95	2.27	10.45	none	−3.24	−24.34	−3.17	−10.45	28.5	47.75
						H$^+$	−3.26	−27.58	−3.18	−11.26		50.89
						SO$_4^{-2}$	−3.28	−24.35	−2.91	−10.45		48.30
b2	5.01	0.22	6.54	3.67	10.61	none	−2.63	−23.27	−2.50	−10.61	−0.4	57.49
						H$^+$	−2.63	−22.86	−2.50	−10.51		57.11
						SO$_4^{-2}$	−2.63	−23.27	−2.50	−10.61		57.49
c2	1.81	0.39	4.94	8.24	11.16	none	−3.05	−25.22	−2.57	−11.16	−0.4	57.49
						H$^+$	−3.05	−25.12	−2.57	−11.14		57.46
						SO$_4^{-2}$	−3.05	−25.22	−2.57	−11.16		57.48
d2	0.42	1.46	7.85	18.6	11.81	none	−3.77	−27.26	−2.41	−11.81	−12.6	57.35
						H$^+$	−3.75	−25.16	−2.40	−11.28		55.34
						SO$_4^{-2}$	−3.72	−27.25	−2.57	−11.81		57.14
e2	0.23	2.10	6.07	28.5	12.21	none	−4.06	−28.71	−2.56	−12.21	−7.85	57.08
						H$^+$	−4.04	−28.22	−2.55	−12.09		56.73
						SO$_4^{-2}$	−4.03	−28.70	−2.76	−12.21		56.69
f2	0.17	1.70	5.31	66.8	12.69	none	−4.32	−30.74	−2.74	−12.69	−5.23	56.70
						H$^+$	−4.42	−32.60	−2.85	−13.18		57.87
						SO$_4^{-2}$	−4.29	−30.73	−3.18	−12.69		55.54
g2	0.14	2.42	6.99	132	12.95	none	−4.55	−31.64	−2.74	−12.95	−1.14	56.61
						H$^+$	−4.54	−31.60	−2.74	−12.93		56.49
						SO$_4^{-2}$						
h2	0.25	2.27	7.74	272	13.18	none	−4.42	−32.60	−2.85	−13.18	−8.37	57.87
						H$^+$	−5.09	−34.86	−2.85	−13.63		54.79
						SO$_4^{-2}$						
i2	0.12	0.8	13.7	672	13.42	none	−4.95	−34.03	−2.83	−13.42	23.0	54.78
						H$^+$	−4.44	−33.70	−3.12	−13.35		56.82
						SO$_4^{-2}$						
j2	0.03	1.23	45.3	1200	13.56	none	−5.71	−34.41	−2.48	−13.59	29.9	52.02
						H$^+$	−5.90	−35.54	−2.51	−13.85		52.19
						SO$_4^{-2}$						

Table 23. Estimation of a solubility product for ettringite (AFt) at 25°C
After analytical data of Warren and Reardon (1994) for undersaturation
conditions and for the first batch of experiments

	Aqueous Characterization (mmol/dm³)					Balance Calculation	Calculated Activities (EQ3NR)				Elec. Imb.	Log K_{sp}
Analysis	[Ca^{+2}]	[Al^{+3}]	[SO$_4^{-2}$]	[Na$^+$]	pH	Option	(Ca^{+2})	(Al^{+3})	(SO$_4^{-2}$)	(H$^+$)	(%)	(25°C)
a1	4.14	0.32	4.06	1.02	10.65	none	−2.66	−23.57	−2.67	−10.65	2.14	57.30
						H$^+$	−2.66	−24.13	−2.67	−10.86		58.09
						SO$_4^{-2}$	−2.66	−23.27	−2.66	−10.65		57.32
b1	3.43	0.4	3.71	1.70	10.74	none	−2.73	−23.53	−2.70	−10.74	0.69	57.35
						H$^+$	−2.73	−23.79	−2.70	−10.81		57.66
						SO$_4^{-2}$	−2.73	−23.53	−2.69	−10.74		57.36
c1	1.88	0.54	3.71	4.34	11.15	none	−3.00	−25.03	−2.67	−11.15	−9.04	57.74
						H$^+$	−2.99	−20.82	−2.67	−10.09		53.64
						SO$_4^{-2}$	−2.98	−25.03	−2.76	−11.15		57.59
d1	0.93	0.88	2.99	5.90	11.51	none	−3.30	−25.26	−2.75	−11.51	−15.6	57.59
						H$^+$	−3.28	−23.81	−2.74	−10.90		55.28
						SO$_4^{-2}$	−3.25	−26.26	−3.00	−11.51		57.08
e1	0.46	1.02	2.81	11.4	12.03	none	−2.81	−25.25	−2.81	−12.03	−21.8	62.54
						H$^+$	−3.62	−26.94	−2.79	−11.69		56.46
						SO$_4^{-2}$						
f1	0.28	1.16	3.03	30.8	12.48	none	−3.98	−30.05	−2.87	−12.48	−16.8	57.14
						H$^+$	−3.94	−29.34	−2.86	−12.31		56.83
						SO$_4^{-2}$						
g1	0.27	1.08	3.42	70.7	12.68	none	−4.10	−30.89	−2.93	−12.68	1.97	56.97
						H$^+$	−4.11	−30.97	−2.93	−12.70		57.02
						SO$_4^{-2}$						
h1	0.29	1.13	3.40	110	12.88	none	−4.17	−31.68	−3.01	−12.88	1.50	57.13
						H$^+$	−4.18	−31.74	−3.02	−12.90		57.22
						SO$_4^{-2}$						
i1	0.31	0.86	4.71	329	13.01	none	−4.26	−32.34	−3.09	−13.01	36.7	56.62
						H$^+$	−4.44	−33.69	−3.12	−13.35		56.83
						SO$_4^{-2}$						
j1	0.2	0.37	20.5	572	13.24	none	−4.61	−33.65	−2.60	−13.24	32.2	56.14
						H$^+$	−4.79	−34.88	−2.63	−13.55		56.23
						SO$_4^{-2}$						

Table 24. Estimation of a solubility product for ettringite (AFt) at 25°C
After analytical data of Warren and Reardon (1994) for undersaturation
conditions and for the second batch of experiments

	Aqueous Characterization (mmol/dm³)					Balance Calculation	Calculated Activities (EQ3NR)				Elec. Imb.	Log K_{sp}
Analysis	[Ca^{+2}]	[Al^{+3}]	[SO$_4^{-2}$]	[Na$^+$]	pH	Option	(Ca^{+2})	(Al^{+3})	(SO$_4^{-2}$)	(H$^+$)	(%)	(25°C)
a2	5.35	0.24	5.29	1.12	10.65	none	−2.58	−23.40	−2.59	−10.65	2.39	57.78
						H$^+$	−2.58	−24.49	−2.59	−10.93		58.95
						SO$_4^{-2}$	−2.58	−23.40	−2.57	−10.65		57.80
b2	3.58	0.40	3.80	1.78	10.83	none	−2.72	−23.88	−2.69	−10.83	0.94	57.83
						H$^+$	−2.72	−24.18	−2.69	−10.90		58.07
						SO$_4^{-2}$	−2.72	−23.88	−2.68	−10.83		57.84
c2	2.02	0.49	3.15	3.98	11.18	none	−2.95	−25.19	−2.74	−11.18	−3.32	57.67
						H$^+$	−2.95	−24.59	−2.74	−11.03		57.28
						SO$_4^{-2}$	−2.94	−25.19	−2.77	−11.18		57.79
d2	0.97	0.94	4.03	9.11	11.69	none	−3.32	−26.96	−2.65	−11.69	−14.6	58.52
						H$^+$	−3.30	−25.19	−2.64	−11.25		56.90
						SO$_4^{-2}$	−3.28	−26.95	−2.88	−11.69		58.07
e2	0.46	1.06	3.00	13.0	12.10	none	−3.67	−28.55	−2.79	−12.10	−22.3	57.71
						H$^+$	−3.63	−27.24	−2.77	−11.77		56.64
						SO$_4^{-2}$						
f2	0.33	0.85	2.60	29.4	12.53	none	−3.92	−30.38	−2.94	−12.53	−22.4	57.23
						H$^+$	−3.86	−29.46	−2.92	−12.30		56.73
						SO$_4^{-2}$						
g2	0.26	1.19	3.40	58.6	12.73	none	−4.13	−31.05	−2.92	−12.73	−12.5	57.15
						H$^+$	−4.08	−30.57	−2.90	−12.62		57.08
						SO$_4^{-2}$						
h2	0.29	1.12	3.72	129.7	12.97	none	−4.21	−32.06	−3.01	−12.97	−0.95	57.23
						H$^+$	−4.21	−32.02	−3.01	−12.96		57.21
						SO$_4^{-2}$						
i2	0.34	0.77	4.67	325	13.20	none	−4.30	−33.16	−3.10	−13.20	16.2	56.96
						H$^+$	−4.39	−33.72	−3.12	−13.34		56.95
						SO$_4^{-2}$						
j2	0.19	0.37	21.4	603	13.33	none	−4.67	−34.01	−2.60	−13.33	25.6	56.09
						H$^+$	−4.82	−34.96	−2.62	−13.57		56.12
						SO$_4^{-2}$						

Table 25.   Estimation of a solubility product for monosulfate (AFm) at 25°C
After analytical data of Atkins et al. (1992, their Table 4.6, p. 26)

Analysis	Aqueous Characterization (mmol/dm³)				Solid Characterization (XRD)	Balance Calculation Option	Calculated Activities (EQ3NR)				Elec. Imb. (%)	Log K_{sp} (25°C)
	$[Ca^{+2}]$	$[Al^{+3}]$	$[SO_4^{-2}]$	$[OH^-]$			(Ca^{+2})	(Al^{+3})	(SO_4^{-2})	(H^+)		
1	7.16	4.10	0.008	22.4		none	−2.47	−28.69	−5.45	−12.28	−33.4	74.65
						H^+	−2.41	−27.24	−5.45	−11.92		73.47
2	6.84	3.52	<0.01	21.0		none	−2.48	−28.64	−5.45	−12.25	−31.7	74.37
						H^+	−2.43	−27.31	−5.44	−11.92		73.28
3	4.71	4.60	<0.01	20.3	AFm	none	−2.63	−28.48	−5.41	−12.24	−48.0	74.02
						H^+						
4	4.94	2.85	0.01	20.9		none	−2.61	−28.74	−5.31	−12.25	−44.4	73.83
						H^+	−2.53	−26.80	−5.30	−11.77		72.23
5	5.05	2.70	0.02	18.7		none	−2.59	−28.57	−5.06	−12.21	−39.0	73.93
						H^+	−2.53	−26.90	−5.04	−11.79		72.55
6	4.42	3.00	0.01	19.9	AFm, AFt	none	−2.65	−28.64	−5.19	−12.23	−47.2	73.76
						H^+	−2.57	−26.46	−5.17	−11.69		71.95
7	4.93	1.60	0.01	19.5		none	−2.60	−28.88	−5.20	−12.23	−43.4	73.37
						H^+	−2.54	−27.33	−5.18	−11.84		72.11

6.2.4 CaO–Al$_2$O$_3$–CO$_2$–H$_2$O System

The presence of CO_2 in the atmosphere or in water implies that cements are, most of the time, in contact with sources of carbonates. The result can be a destabilization of the following main hydrates and a degradation of the cement:

- C–S–H gel can be transformed into a mixture of silica gel and calcite.
- C_3AH_6 will evolve toward calcium monocarboaluminate, and thereafter to a mixture of gibbsite and calcite.
- C_4AH_{13} will be transformed into calcium hemicarboaluminate, then calcium monocarboaluminate, and finally calcite and gibbsite.

These degradation products must be introduced in the data file as well.

Calcite. The CaO–CO$_3$–H$_2$O closed system was studied in particular by Plummer et al. (1982) and Cowie et al. (1992). The only form of $CaCO_3$ taken into account is calcite because it is the only stable form at 25°C. The coexistence of portlandite and calcite corresponds to the invariant point [Ca] = 21.95 mol/L and [CO$_3$] = 6.93 mmol/L (Damidot et al., 1994). The composition of a solution in equilibrium with these two minerals calculated by EQ3NR gives the results shown in Table 26.

Table 26. Composition and characteristics of a fluid in equilibrium with calcite and portlandite

Element	Molality	Log Activity
Ca^{+2}	1.33×10^{-2}	−2.1855
CO_3^{-2}	8.80×10^{-4}	−3.3603

Description of the Solution		Solids	
pH	12.35	Calcite	Log Q/K = 2.934
Ionic strength	0.043	Portlandite	Log Q/K = −0.034
Temperature	25°C		
Density of H_2O	1		
Electrical balance	0.29×10^{-6}		

Hemicarboaluminate and Monocarboaluminate. Solubility experiments carried out at 25°C by Damidot et al. (1994) were used to derive solubility products for these two phases. The results are shown in Table 27.

Table 27. Calculation of a solubility product for hemicarboaluminate and monocarboaluminate at 25°C
After analytical data of Damidot et al. (1994)

Hydrate	Experimental Data (mmol/l)				Imbalance	Calculated Activities (EQ3NR)				Log
	$[Ca^{+2}]$	$[Al^{+3}]$	$[CO_3^{-2}]$	pH	(%)	$[Ca^{+2}]$	$[Al^{+3}]$	$[HCO_3^-]$	$[H^+]$	K_{sp}
Hemicarbo-aluminate	4.22	2.02	0.72	11.62	1.03	−2.63	−26.33	−5.25	−11.62	80.74
Monocarbo-aluminate	2.72	1.39	0.90	11.30	0.38	−2.83	−25.21	−4.68	−11.30	80.48

The dissolution reactions considered here were written as follows:

$$\text{Hemicarboaluminate} + 12.5\,H^+ \rightarrow 3.5\,Ca^{+2} + 2\,Al^{+3} + 0.5\,HCO_3^- + 16.5\,H_2O ; \qquad (7)$$

$$\text{Monocarboaluminate} + 13\,H^+ \rightarrow 4\,Ca^{+2} + 2\,Al^{+3} + HCO_3^- + 16\,H_2O . \qquad (8)$$
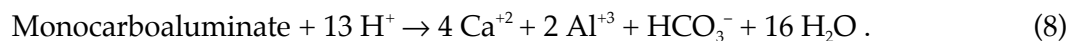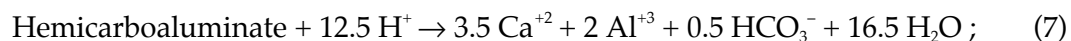
Gibbsite. Table 28 lists the thermodynamic data for gibbsite given in the COM data file.

Table 28. Thermodynamic data for gibbsite given in the COM data file

```
Gibbsite          Al(OH)3
    date last revised = 08-aug-1984
    keys = solid   polymorph
        V0PrTr = 31.956 cm**3/mol (source = supcrt92 )
*   mwt = 78.00356 g/mol
     3 chemical elements =
    1.0000 Al      3.0000 H           3.0000 O
    4 species in data0 reaction
    −1.0000 Gibbsite         −3.0000 H+
    1.0000 Al+++            3.0000 H2O
*    log k grid (0-25-60-100/150-200-250-300 C) =
        8.2578  6.7965  5.1162  3.5871
        2.0647  0.8088  −0.3021 −1.3483
*   Extrapolation algorithm: supcrt92
*   gflag = 1 (supcrt92 equations and data used)
*   basic source = supcrt92
*   delG0f = −276.168 kcal/mol
*   delH0f = −309.065 kcal/mol
*   S0PrTr = 16.750 cal/(mol*K)
*   cp coefficients (source = supcrt92)
*   T**0 = 0.86500000E+01
*   T**1 = 0.45600000E-01
*   T**-2 = 0.00000000E+00
*   Tlimit = 151.85 C
```

Amorphous silica. Table 29 lists the thermodynamic data for amorphous silicate given in the COM data file.

Table 29. Thermodynamic data for amorphous silica given in the COM data file

```
SiO2(am)
     date last revised = 06-mar-1990
    keys = solid   polymorph
        V0PrTr = 29.000 cm**3/mol (source = supcrt92)
*       mwt = 60.08430 g/mol
     2 chemical elements =
    2.0000 O      1.0000 Si
     2 species in data0 reaction
    −1.0000 SiO2(am)      1.0000 SiO2(aq)
*    log k grid (0-25-60-100/150-200-250-300 C) =
        −3.1240  −2.7136  −2.4067  −2.1843
        −1.9796  −1.8190  −1.6928  −1.6042
*   Extrapolation algorithm: supcrt92
*   gflag = 1 (supcrt92 equations and data used)
*   basic source = supcrt92
*   delG0f = −202.892 kcal/mol
*   delH0f = −214.568 kcal/mol
*   S0PrTr = 14.340 cal/(mol*K)
*   cp coefficients (source = supcrt92)
*   T**0 = 0.59300000E+01
*   T**1 = 0.47200000E-01
* T**-2 = -0.22780000E+07
* Tlimit = 348.85 C
```

6.2.5 CaO–Al$_2$O$_3$–SiO$_2$–SO$_3$–H$_2$O System

The phase considered in this study is gehlenite hydrate (Ca$_2$Al$_2$SiO$_{7.8}$H$_2$O). Atkins et al. (1991) (see Table 30) found it impossible to synthesize pure gehlenite hydrate because C$_3$ASH$_4$ was always present as an impurity. However, their report provides analytical results of interest (see their Table 4.7, p. 27), from which a solubility product is derived here. As for other phases, such as the monosulfate and C$_4$AH$_{13}$, this type of calculation is not thermodynamically valid.

A value of 49.84 was introduced in the COM data file. This value corresponds to the average of the activity products for the first six experimental results. The last two in the series show some discrepancy with the rest of the data and are thus not taken into account.

Table 30. Estimation of a solubility product for gehlenite hydrate at 25°C
After analytical data of Atkins et al. (1992, their Table 4.7, p. 27)

Analysis	Aqueous Characterization (mmol/dm^3)				Solid Characterization (XRD)	Balance Calculation Option	Calculated Activities (EQ3NR)				Elec. Imb. (%)	Log K_{sp} (25°C)
	[Ca^{+2}]	[Al^{+3}]	[SiO$_2$]	[OH$^-$]			(Ca^{+2})	(Al^{+3})	(SiO$_{2(aq)}$)	(H$^+$)		
1	2.00	0.97	<0.04	6.5		none	−2.88	−27.13	−6.26	−11.74	−29.2	51.13
						H$^+$	−2.85	−25.88				
2	1.50	0.95	0.01	4.8		none	−2.98	−26.65	−6.58	−11.62	−30.7	50.35
						H$^+$	−2.98	−25.23				
3	1.28	0.74	0.02	4.3	C$_2$ASH$_8$ +	none	−3.04	−26.68	−6.45	−11.60	−34.1	50.11
						H$^+$	−3.04	−25.14				
4	1.09	0.77	0.02	4.15	C$_3$ASH$_4$ (impurity)	none	−3.10	−26.58	−6.36	−11.58	−39.5	50.07
						H$^+$	−3.11	−24.82				
5	1.00	0.58	0.02	3.8		none	−3.13	−26.46	−6.26	−11.52	−36.2	49.75
						H$^+$	−3.07	−24.68				
6	0.91	0.61	0.03	4.0		none	−3.17	−26.56	−6.22	−11.55	−43.0	49.81
						H$^+$	−3.14	−24.51				
7	0.36	0.29	0.06	1.31		none	−3.53	−25.07	−5.46	−11.10	−40.1	48.34
						H$^+$	−3.51	−22.92				
8	0.17	0.17	0.07	pH = 9.2		none	−3.81	−17.69	−4.23	−9.2	25.7	44.77
						H$^+$	−3.81	−21.22				

7. Summary

This report documents the process by which thermodynamic data from the extant literature has been rendered into a form that can be used by the EQ3/6 modeling package. The purpose of adding the new data is to increase our simulation capabilities in the area of materials, cement in particular. If the thermodynamic data for a particular mineral phase is not present in the database, it is not possible to account for that phase in the simulation. Our new database allows us to take a major step forward in modeling the interaction between cement and water at 25°C. Additional work remains to be done to include some of those phases expected to participate in chemical reactions between cement and water at elevated temperature.

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Appendix A

Notation for Cement Chemistry

The following notation, widely used by cement chemists, is incorporated into the present report:

$$A = Al_2O_3$$
$$C = CaO$$
$$\underline{C} = CO_3$$
$$F = Fe_2O_3$$
$$H = H_2O$$
$$K = K_2O$$
$$M = MgO$$
$$N = Na_2O$$
$$S = SiO_2$$
$$\underline{S} = SO_3$$
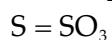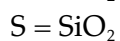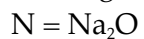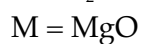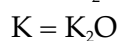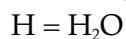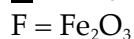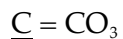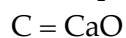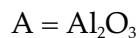
Compounds and abbreviations of particular note are:

AFt   ettringite
AFm   monosulfate
bfs   blast-furnace slag
C–S–H   calcium silicate hydrate
OPC   ordinary Portland cement

Appendix B

Cement Paste Reactant File Used for Simulating the Composition of Aqueous Phases in Contact with an OPC Paste

```
|--------------------------------------------------------------------|
| input file name = cement_dw_25_5D.6i                               |
|        revisor = laurence                                          |
|           date = 11/15/95                                          |
|                                                                    |
|                                                                    |
|--------------------------------------------------------------------|
| calculational mode  |*normal     | economy          | super economy|
|--------------------------------------------------------------------|
| model type          | titration  |*closed           | open         |
|--------------------------------------------------------------------|
| temperature model   |*power      | fluid mixing                    |
|--------------------------------------------------------------------|
c power model  -->   temp = tstart + tk1*zi + tk2*zi**2 + tk3*zi**3  |
c mixing model -->   temp = (tstart * tk1 + zi*tk2) / (zi + tk1)     |
c--------------------------------------------------------------------|
| tstart(c)| 25.00   |tk1|    0.   |tk2|     0.   |tk3|     0.        |
|--------------------------------------------------------------------|
| starting value of zi |     0.   |max. value of zi    | 1.0000       |
|--------------------------------------------------------------------|
| starting time (sec)  |     0.   |max. time (sec)     | 1.00000e+38  |
|--------------------------------------------------------------------|
| max. steps           |    1000  |max. steps w/o print|     1000    |
|--------------------------------------------------------------------|
| linear print interval| 1.00000e+05|log print interval | 0.50000    |
|--------------------------------------------------------------------|
| suppress mineral phases                                            |
|--------------------------------------------------------------------|
| phases w/ elements|                        |                      |n
| phases except     |                        |                      |n
|--------------------------------------------------------------------|
| fixed fugacity phases- species, moles(per kg h2o), log fugacity(bars)|
|--------------------------------------------------------------------|
| CO2(g)                          | 20.0         | -30.0             |
|--------------------------------------------------------------------|
c                R A T E    L A W S
c 1 = relative                 rate = rk1 + rk2*zi + (1/2)rk3*zi*zi
c 2 = transition state theory  rate = sk*fk*SUM( rk(i)*PROD(ACT*cdac(i))
c                                      (1-exp(AFF/(csigma(i)*R*T)) )
c                                      where i = 1,4
c 3 = two term linear-parabolic rate = (rk1+rk2*(rk3-time)**.5)
c 4 = activity term rate              see manual
c 5 = affinity to a power       rate = fk*sk*rk1*aff**rk2
c
c                R E A C T A N T    T Y P E S
c mineral    solid solution     special    aqueous    gas
c
c                S U R F A C E    T Y P E
c 0 = fixed surface area    1 = fixed specific surface area
c
c                N O T E S
c status and jreac are normally not set by the user
|--------------------------------------------------------------------|
| reactants  (ss) solid solution only    (sp) special reactant only  |
|--------------------------------------------------------------------|
```

```
| REACTANT          | CSH17gel          |status  | 0            |
| moles remaining   |   0.1790          |destroyed|     0.      |
| reactant type     | mineral           |sk      |      0.     |
| surface type      |   0               |fk      |   1.0000     |
| DISSOLUTION LAW   |   1               |        |              |
| rate constant rk1|  100.0000          |csigma1 |              |
| PRECIPITATION LAW|    0               |        |              |
c-------------------------------------------------------------------|
| REACTANT          | Portlandite       |status  | 0            |
| moles remaining   |   0.2450          |destroyed|     0.      |
| reactant type     | mineral           |sk      |      0.     |
| surface type      |   0               |fk      |   1.0000     |
| DISSOLUTION LAW   |   1               |        |              |
| rate constant rk1|  100.0000          |csigma1 |              |
| PRECIPITATION LAW|    0               |        |              |
c-------------------------------------------------------------------|
| REACTANT          | Calcite           |status  | 0            |
| moles remaining   |   0.0260          |destroyed|     0.      |
| reactant type     | mineral           |sk      |      0.     |
| surface type      |   0               |fk      |   1.0000     |
| DISSOLUTION LAW   |   1               |        |              |
| rate constant rk1|  100.0000          |csigma1 |              |
| PRECIPITATION LAW|    0               |        |              |
c-------------------------------------------------------------------|
| REACTANT          | Ettringite        |status  | 0            |
| moles remaining   |   0.0150          |destroyed|     0.      |
| reactant type     | mineral           |sk      |      0.     |
| surface type      |   0               |fk      |   1.0000     |
| DISSOLUTION LAW   |   1               |        |              |
| rate constant rk1|  100.0000          |csigma1 |              |
| PRECIPITATION LAW|    0               |        |              |
c-------------------------------------------------------------------|
| REACTANT          | Ca3Al2O6:6H2O     |status  | 0            |
| moles remaining   |   0.0100          |destroyed|     0.      |
| reactant type     | mineral           |sk      |      0.     |
| surface type      |   0               |fk      |   1.0000     |
| DISSOLUTION LAW   |   1               |        |              |
| rate constant rk1|  100.0000          |csigma1 |              |
| PRECIPITATION LAW|    0               |        |              |
|-------------------------------------------------------------------|
| options                                                           |
|-------------------------------------------------------------------|
| - SOLID SOLUTIONS -                                               |
|    * ignore solid solutions                                       |
|      process solid solutions                                      |
| - LOADING OF SPECIES INTO MEMORY -                                |
|    * don't print                                                  |
|      lists species loaded into memory                             |
| - LIST DERIVATIVES OF BASIS ELEMENTS AT EACH PRINT POINT -        |
|    * don't print                                                  |
|      print                                                        |
| - LIST ALL SPECIES LOADED INTO MEMORY AND THEIR LOG K VALUES -    |
|    * don't print                                                  |
|      print                                                        |
| - LIST DISTRIBUTION OF AQUEOUS SPECIES AT EACH PRINT POINT -      |
|      only species > 10**-12 molal                                 |
|      all species                                                  |
|    * don't print                                                  |
| - LIST CATION/H+ ACTIVITY RATIOS AT EACH PRINT POINT -            |
|    * don't print                                                  |
|      print                                                        |
| - LIST BULK ELEMENT AND OXIDE COMPOSITION AT EACH PRINT POINT -   |
|      don't print                                                  |
|    * print                                                        |
```

```
| - MINERAL SATURATION STATES -                                        |
|     print if affinity > -10 kcals                                    |
|     print all                                                        |
|   * don't print                                                      |
| - LIST GAS SPECIES SUMMARY AT EACH PRINT POINT -                     |
|   * don't print                                                      |
|     print                                                            |
| - PRINT AQUEOUS MASS AND CONCENTRATION TOTALS -                      |
|     don't print                                                      |
|   * print                                                            |
| - TAB FILES -                                                        |
|   * write                                                            |
|     append to previous tabx file                                     |
|     don't write                                                      |
| - WRITE PICKUP FILE -                                                |
|   * write pickup file at end of run                                  |
|     don't write pickup file                                          |
|     write pickup file for each print point                           |
| - PHYSICALLY REMOVED SUBSYSTEM -                                     |
|   * does nothing                                                     |
|     transfer minerals but leave trivial mass in the system           |
|     transfer minerals                                                |
| - CLEAR INITIAL PHYSICALLY REMOVED SUBSYSTEM -                        |
|   * does nothing                                                     |
|     clear p.r.s. before first reaction progress advance              |
| - PHASE BOUNDARY SEARCH -                                            |
|   * step size constrained by predicted phase boundaries              |
|     phase boundaries estimated from Taylor's series and printed       |
|     locations of phase boundaries ignored                            |
| - AUTO BASIS SWITCHING -                                            |
|   * off                                                              |
|     on                                                               |
| - SUPPRESS REDOX REACTIONS -                                        |
|   * does nothing                                                     |
|     suppress all redox reactions                                     |
| - LINEAR OR LOGARITHMIC TAYLOR'S SERIES -                            |
|   * linear for kcol = 1,kdim, logarithmic for kcol = 1,kbt           |
|     logarithmic for kcol = 1,kbt                                     |
|     linear for kcol = 1,kdim                                         |
| - AZERO AND HYDRATION NUMBERS -                                     |
|   * no change                                                        |
|     read in new azero and hydration numbers                          |
| - PRINT MEAN MOLAL ACTIVITY COEFFICIENTS FOR DISSOLVED SPECIES -     |
|   * does nothing                                                     |
|     print                                                            |
| - PITZER DATABASE INFORMATION -                                     |
|   * print only warnings                                             |
|     print species in model and number of Pitzer coefficients         |
|     print species in model and names of Pitzer coefficients          |
| - PRINT DIAGNOSTIC MESSAGES -                                       |
|   * don't print                                                      |
|     print level 1 messages                                          |
|     print level 2 messages                                          |
| - PRINT PRE-NEWTON-RAPHSON OPTIMIZATION -                           |
|   * don't print                                                      |
|     print summary information                                        |
|     print detailed information                                       |
| - PRINT STEP SIZE AND ORDER -                                       |
|   * don't print                                                      |
|     print scale factor                                               |
|     print orders and step size scaling factors                       |
| - CONTROL STEP SIZE AND ORDER PRINT -                               |
|   * does nothing                                                     |
|     print step size and order when delzi .le. dlzmx1                 |
```

```
| - NEWTON ITERATIONS -                                                   |
|   * don't print                                                         |
|     print summary of newton iterations                                  |
|     print summary, residual functions and correction terms              |
|     print summary, residual functions, correction terms and matrix      |
| - PRINT SEARCH ITERATIONS -                                             |
|   * don't print                                                         |
|     print                                                               |
| - PRINT HPSAT ITERATIONS -                                             |
|   * don't print                                                         |
|     print                                                               |
| - PRINT FINITE DIFFERENCE AND DERIVATIVE DATA -                        |
|   * don't print                                                         |
|     print computations from RDERIV, and RTAYLR                          |
|     print computations from RDERIV, RTAYLR, DERIV and TAYLOR            |
| - PRINT KINETICS DIAGNOSTIC MESSAGES -                                 |
|   * don't print                                                         |
|     print level 1 diagnostics                                           |
|     print level 1 and level 2 diagnostics                               |
| - PRINT AKMATR -                                                        |
|   * don't print                                                         |
|     print level 1 diagnostics                                           |
| - KILL ITERATION VARIABLES -                                           |
|   * does nothing                                                        |
|     allow selection of variables to remove                              |
|-------------------------------------------------------------------------|
| development options  (used for code development)                        |
|-------------------------------------------------------------------------|
|    0 check finite difference and Taylor series expression               |
|    0 check reaction rate finite difference and Taylor series            |
|-------------------------------------------------------------------------|
| tolerances                      desired values - defaults info-only      |
|-------------------------------------------------------------------------|
| number of N-R iterations       |       30        |  30      itermx      |
| p.r.s. transfer interval       | 1.00000e+38     |  varies  dlzidp      |
| residual magnitude             | 1.00000e-06     |  1.0e-06 tolbt       |
| correction magnitude           | 1.00000e-06     |  1.0e-06 toldl       |
| search/find tolerance          | 1.00000e-06     |  varies  tolx        |
| supersaturation                | 5.00000e-05     |  varies  tolsat      |
| supersaturation set size       | 1.00000e-04     |  varies  tolsst      |
| max. size Taylor's series term | 0.50000e-04     |  1.0e-04 screw1      |
| max. initial value betamx      | 0.50000         |  n/a     screw2      |
| max. Taylor's series term (kin.)| 1.00000e-05    |  1.0e-04 screw3      |
| corrector iteration            | 1.00000e-04     |  1.0e-04 screw4      |
| max. size of N-R correction term  2.0000         |  4.0     screw5      |
| step size (economy mode)       | 2.0000          |  4.0     screw6      |
| log mass of phases             |                 |  varies  zklogu      |
| decrement mass (p.r.s.)        | 2.0000          |  2.0     zklogl      |
| min. left after p.r.s.         |                 |  .98     zkfac       |
| initial step size              |                 |  varies  dlzmx1      |
| upper limit step size          | 1.00000e+38     |  varies  dlzmx2      |
| maximum order                  |                 |  6       nordlm      |
| num. attempted assemblages     |       25        |  25      ntrymx      |
| slide -> over phase bound.     |       30        |  8       npslmx      |
| slide -> over redox insta.     |        3        |  3       nsslmx      |
| fo2 scan control               |                 |  none    ioscan      |
|-------------------------------------------------------------------------|
c pickup file written by EQ3NR.7.2bR139                                   |
c supported by eqlib.7.2bR168                                             |
|EQ3NR input file name= sol_cement.3i                                    |          |
|                                                                         |
|                                                                         |
|-------------------------------------------------------------------------|
| temperature (C)                |       25.000    |                       |
|-------------------------------------------------------------------------|
```

```
| electrical imbalance             |   2.668182341736269E-11      |
|-----------------------------------------------------------------|
| number of aqueous master species |    10                        |
|-----------------------------------------------------------------|
| position of last pure mineral    |    10                        |
|-----------------------------------------------------------------|
| position of last solid solution  |    10                        |
|-----------------------------------------------------------------|
| suppressed species     (suppress,replace,augmentk,augmentg)  value |
|-----------------------------------------------------------------|
| none                   |                                        |
|-----------------------------------------------------------------|
| iopg options                                                    |
|-----------------------------------------------------------------|
| - pH SCALE CONVENTION -                                         |
|    * modified NBS                                               |
|      internal                                                   |
|      rational                                                   |
| - ACTIVITY COEFFICIENT OPTIONS -                                |
|    * use B-dot equation                                         |
|      Davies' equation                                           |
|      Pitzer's equations                                         |
|-----------------------------------------------------------------|
| elements, moles and moles aqueous                               |
|-----------------------------------------------------------------|
| O              | 5.568776506755892E+01 | 0.000000000000000E+00 |
| Al             | 6.370000001481312E-04 | 0.000000000000000E+00 |
| C              | 1.426798063709184E-04 | 0.000000000000000E+00 |
| Ca             | 4.000000000345726E-04 | 0.000000000000000E+00 |
| H              | 1.111868479754670E+02 | 0.000000000000000E+00 |
| K              | 9.490000000028020E-02 | 0.000000000000000E+00 |
| Na             | 7.700000000007631E-02 | 0.000000000000000E+00 |
| S              | 9.000000001046448E-04 | 0.000000000000000E+00 |
| Si             | 1.782999999526204E-03 | 0.000000000000000E+00 |
|-----------------------------------------------------------------|
| master species and logarithmic basis variables                 |
|-----------------------------------------------------------------|
| H2O            | H2O              |  1.744358983526984E+00 |
| Al+++          | Al+++            | -3.187020707533198E+01 |
| HCO3-          | HCO3-            | -6.976044604027794E+00 |
| Ca++           | Ca++             | -3.656844272487772E+00 |
| H+             | H+               | -1.298227656893866E+01 |
| K+             | K+               | -1.035812903953679E+00 |
| Na+            | Na+              | -1.117296945881325E+00 |
| SO4--          | SO4--            | -3.173787535244035E+00 |
| SiO2(aq)       | SiO2(aq)         | -6.759755466584413E+00 |
| O2(g)          | O2(g)            | -7.000000000000000E-01 |
|-----------------------------------------------------------------|
| physically removed subsystem  (solid solution, mineral, moles)  |
|-----------------------------------------------------------------|
| none           |                  |                  |          |
|-----------------------------------------------------------------|
```

Appendix C

SUP* Datafile SLIST

EQPT Species List File:

```
no. of elements on the data file          =    69
         the dimensioned limit            =   100
no. of aqueous species in the master set =   135
         the dimensioned limit            =   500


data0.sup.R22a
 YMP Configuration Item Identifier: DATA0-V7-SUP-R22a
 a. Modifications by T. Wolery 12/10/93
    1. Name of O2(g) changed from "Oxygen" to "O2(g)"
    2. Name of H2(g) changed from "Helium" to "H2(g)"
 THERMODYNAMIC DATABASE
 generated by gembochs/INGRES  12-jul-93
 +-----------------------------------------------
```

```
element = O        , atwt =   15.99940          element = N        , atwt =   14.00674
element = Ag       , atwt =  107.86820          element = Na       , atwt =   22.98977
element = Al       , atwt =   26.98154          element = Nd       , atwt =  144.24000
element = Ar       , atwt =   39.94800          element = Ne       , atwt =   20.17970
element = Au       , atwt =  196.96654          element = Ni       , atwt =   58.69000
element = B        , atwt =   10.81100          element = Pb       , atwt =  207.20000
element = Ba       , atwt =  137.32700          element = Pd       , atwt =  106.42000
element = Be       , atwt =    9.01218          element = Pr       , atwt =  140.90765
element = Br       , atwt =   79.90400          element = Ra       , atwt =  226.02500
element = Ca       , atwt =   40.07800          element = Rb       , atwt =   85.46780
element = Cd       , atwt =  112.41100          element = Re       , atwt =  186.20700
element = Ce       , atwt =  140.11500          element = Rn       , atwt =  222.00000
element = Cl       , atwt =   35.45270          element = S        , atwt =   32.06600
element = Co       , atwt =   58.93320          element = Sc       , atwt =   44.95591
element = Cr       , atwt =   51.99610          element = Se       , atwt =   78.96000
element = Cs       , atwt =  132.90543          element = Si       , atwt =   28.08550
element = Cu       , atwt =   63.54600          element = Sm       , atwt =  150.36000
element = Dy       , atwt =  162.50000          element = Sn       , atwt =  118.71000
element = Er       , atwt =  167.26000          element = Sr       , atwt =   87.62000
element = Eu       , atwt =  151.96500          element = Tb       , atwt =  158.92534
element = F        , atwt =   18.99840          element = Tl       , atwt =  204.38330
element = Fe       , atwt =   55.84700          element = Tm       , atwt =  168.93421
element = Ga       , atwt =   69.72300          element = V        , atwt =   50.94150
element = Gd       , atwt =  157.25000          element = W        , atwt =  183.85000
element = H        , atwt =    1.00794          element = Xe       , atwt =  131.29000
element = As       , atwt =   74.92159          element = Y        , atwt =   88.90585
element = C        , atwt =   12.01100          element = Yb       , atwt =  173.04000
element = P        , atwt =   30.97362          element = Zn       , atwt =   65.39000
element = He       , atwt =    4.00206
element = Hg       , atwt =  200.59000
element = Ho       , atwt =  164.93032
element = I        , atwt =  126.90447
element = In       , atwt =  114.82000
element = K        , atwt =   39.09830
element = Kr       , atwt =   83.80000
element = La       , atwt =  138.90550
element = Li       , atwt =    6.94100
element = Lu       , atwt =  174.96700
element = Mg       , atwt =   24.30500
element = Mn       , atwt =   54.93085
element = Mo       , atwt =   95.94000
```

Aqueous

1 H2O	Ag+
3 Al+++	Ar(aq)
5 Au+	B(OH)3(aq)
7 Ba++	Be++
9 Br-	Ca++
11 Cd++	Ce+++
13 Cl-	Co++
15 CrO4--	Cs+
17 Cu++	Dy+++
19 Er+++	Eu+++
21 F-	Gd+++
25 H+	H2AsO4-
27 HCO3-	HPO4--
29 He(aq)	Hg++
31 Ho+++	I-
33 In+++	K+
35 Kr(aq)	La+++
37 Li+	Lu+++
39 Mg++	Mn++
41 MoO4--	NO3-
43 Na+	Nd+++
45 Ne(aq)	Ni++
47 Pb++	Pd++
49 Pr+++	Ra++
51 Rb+	ReO4-
53 Rn(aq)	SO4--
55 Sc+++	SeO3--
57 SiO2(aq)	Sm+++
59 Sn++	Sr++
61 Tb+++	Tl+
63 Tm+++	VO++
65 WO4--	Xe(aq)
67 Y+++	Yb+++
69 Zn++	O2(g)
71 HS-	NH4+
73 Acetic acid(aq)	S2--
75 S2O3--	Acetone(aq)
77 Ag++	Au+++
79 BF4-	Benzene(aq)
81 Br3-	BrO-
83 BrO3-	BrO4-
85 Butanoic acid(aq)	CN-
87 ClO-	ClO2-
89 ClO3-	ClO4-
91 Co+++	Cu+
93 Ethane(aq)	Eu++
95 Fe+++	Formic acid(aq)
97 Glycine(aq)	H2(aq)
99 H2AsO3-	H2PO4-
101 H2VO4-	H3P2O7-
103 HSO5-	HSe-
105 Hg2++	I3-
107 IO-	IO3-
109 IO4-	Methanamine(aq)
111 Methane(aq)	Methanol(aq)
113 MnO4--	N2(aq)
115 NO2-	O2(aq)
117 PO4---	Propanoic acid(aq)
119 S2O4--	S2O5--
121 S2O6--	S2O8--

123 S3--	S3O6--
125 S4--	S4O6--
127 S5--	S5O6--
129 SO3--	SeO4--
131 SiF6--	Sm++
133 Tl+++	VO2+
135 Yb++	1-Butanamine(aq)
137 1-Butanol(aq)	1-Butene(aq)
139 1-Butyne(aq)	1-Heptanamine(aq)
141 1-Heptanol(aq)	1-Heptene(aq)
143 1-Heptyne(aq)	1-Hexanamine(aq)
145 1-Hexanol(aq)	1-Hexene(aq)
147 1-Hexyne(aq)	1-Octanamine(aq)
149 1-Octanol(aq)	1-Octene(aq)
151 1-Octyne(aq)	1-Pentanamine(aq)
153 1-Pentanol(aq)	1-Pentene(aq)
155 1-Pentyne(aq)	1-Propanamine(aq)
157 1-Propanol(aq)	1-Propene(aq)
159 1-Propyne(aq)	2-Butanone(aq)
161 2-Heptanone(aq)	2-Hexanone(aq)
163 2-Octanone(aq)	2-Pentanone(aq)
165 Acetate	Ag(CO3)2---
167 AgCO3-	AgCl(aq)
169 AgCl2-	AgCl3--
171 AgCl4---	AgNO3(aq)
173 AlO2-	AlOH++
175 Alanine(aq)	Asparagine(aq)
177 Aspartic acid(aq)	BO2-
179 BaCO3(aq)	BaCl+
181 BaF+	BaHCO3+
183 BeO2--	Butanoate
185 CO2(aq)	CO3--
187 CaCO3(aq)	CaCl+
189 CaCl2(aq)	CaF+
191 CaHCO3+	CaSO4(aq)
193 CoOH+	Cr2O7--
195 CsBr(aq)	CsCl(aq)
197 CsI(aq)	Ethanamine(aq)
199 Ethanol(aq)	Ethylbenzene(aq)
201 Ethylene(aq)	Ethyne(aq)
203 Fe(CH3COO)2(aq)	FeCH3COO+
205 FeCl+	FeCl2(aq)
207 FeO(aq)	FeOH+
209 Formate	Glutamic acid(aq)
211 Glutamine(aq)	H2P2O7--
213 H2S(aq)	H3PO4(aq)
215 HAsO4--	HCrO4-
217 HF(aq)	HF2-
219 HFeO2-	HNIO2-
221 HNO3(aq)	HO2-
223 HPbO2-	HSO3-
225 HSO4-	HSeO3-
227 HSeO4-	HSiO3-
229 HVO4--	HZnO2-
231 Heptanoate	Heptanoic acid(aq)
233 Hexanoate	Hexanoic acid(aq)
235 Isoleucine(aq)	KBr(aq)
237 KCl(aq)	KHSO4(aq)
239 KI(aq)	KOH(aq)
241 KSO4-	Leucine(aq)
243 LiCl(aq)	Methionine(aq)
245 MgCO3(aq)	MgCl+
247 MgF+	MgHCO3+
249 MgOH+	MnCl+

251	MnO4-	MnSO4(aq)
253	NH3(aq)	NaBr(aq)
255	NaCl(aq)	NaF(aq)
257	NaHSiO3(aq)	NaI(aq)
259	NiCl+	NiO(aq)
261	NiOH+	OH-
263	Octanoate	Octanoic acid(aq)
265	Pb(CH3COO)2(aq)	PbCH3COO+
267	PbCl+	PbCl2(aq)
269	PbCl3-	PbCl4--
271	PbO(aq)	PbOH+
273	Pentanoate	Pentanoic acid(aq)
275	Phenol(aq)	Phenylalanine(aq)
277	Propane(aq)	Propanoate
279	RbBr(aq)	RbCl(aq)
281	RbF(aq)	RbI(aq)
283	SO2(aq)	Serine(aq)
285	SrCO3(aq)	SrCl+
287	SrF+	SrHCO3+
289	Threonine(aq)	Toluene(aq)
291	Tryptophan(aq)	Tyrosine(aq)
293	Valine(aq)	Zn(CH3COO)2(aq)
295	Zn(CH3COO)3-	ZnCH3COO+
297	ZnCl+	ZnCl2(aq)
299	ZnCl3-	ZnCl4--
301	ZnO(aq)	ZnO2--
303	ZnOH+	a-Aminobutyric acid(aq)
305	n-Butane(aq)	n-Butylbenzene(aq)
307	n-Heptane(aq)	n-Heptylbenzene(aq)
309	n-Hexane(aq)	n-Hexylbenzene(aq)
311	n-Octane(aq)	n-Octylbenzene(aq)
313	n-Pentane(aq)	n-Pentylbenzene(aq)
315	n-Propylbenzene(aq)	

Minerals

1	Acanthite	Silver
3	Akermanite	Alabandite
5	Albite	Albite high
7	Albite low	Alunite
9	Analcime#1	Analcime-dehy#1
11	Andalusite	Andradite
13	Anglesite	Anhydrite
15	Annite	Anorthite
17	Anthophyllite	Antigorite
19	Aragonite	Artinite
21	Gold	Azurite
23	Barite	Berndtite
25	Boehmite	Bornite
27	Brucite	Bunsenite
29	Graphite	Ca-Al Pyroxene
31	Calcite	Cassiterite
33	Celestite	Cerussite
35	Chalcedony	Chalcocite
37	Chalcopyrite	Chlorargyrite
39	Chrysotile	Cinnabar
41	Clinochlore-14A	Clinochlore-7A
43	Clinozoisite	Coesite
45	Cordierite anhyd	Cordierite hydr
47	Corundum	Covellite
49	Cristobalite	Cristobalite-a
51	Cristobalite-b	Copper

53	Cuprite	Diaspore
55	Diopside	Dolomite
57	Dolomite-dis	Dolomite-ord
59	Enstatite	Epidote
61	Epidote-ord	Fayalite
63	Iron	FeO
65	Ferrosilite	Fluorite
67	Forsterite	Galena
69	Gehlenite	Gibbsite
71	Grossular	Halite
73	Hedenbergite	Hematite
75	Herzenbergite	Huntite
77	Hydromagnesite	Jadeite
79	K-Feldspar	K2O
81	Kalsilite	Kaolinite
83	Kyanite	Laumontite
85	Lawsonite	Lime
87	Magnesite	Magnetite
89	Malachite	Manganosite
91	Margarite	Maximum Microcline
93	Merwinite	Metacinnabar
95	Monticellite	Muscovite
97	Na2O	Nepheline
99	Nesquehonite	Nickel
101	Paragonite	Pargasite
103	Periclase	Phlogopite
105	Prehnite	Pyrite
107	Pyrophyllite	Pyrrhotite
109	Quartz	Rhodochrosite
111	Romarchite	Sanidine high
113	Sepiolite	SiO2(am)
115	Siderite	Sillimanite
117	Smithsonite	Tin
119	Sphalerite	Spinel
121	Strontianite	Sylvite
123	Talc	Tenorite
125	Tremolite	Wairakite
127	Witherite	Wollastonite
129	Wurtzite	Zoisite

Liquids

1 Quicksilver
 * note - (eqpt/pcrsg) The pure liquids block
has not been written on the data1 and data1f
files, because the EQ3NR and EQ6 codes
presently do not treat non-aqeuous liquids.

Gases

1	Argon	CH4(g)
3	CO2(g)	H2(g)
5	H2O(g)	H2S(g)
7	Helium	Krypton
9	Nitrogen	NH3(g)
11	Neon	O2(g)
13	Radon	S2(g)
15	SO2(g)	Xenon

Solid Solutions

0 none

Appendix D

Minerals Present in the COM Datafile
and to Be Added to the SUP* Datafile

```
+----------------------------------------------------------------
Afwillite               Ca3Si2O4(OH)6
     sp.type =  solid
*    EQ3/6   =  com, alt
     revised =  27-mar-1990
*    mol.wt. =   342.447 g/mol
     V0PrTr  =   129.230 cm**3/mol [source: 86jen    ]
****
     4 element(s):
      3.0000 Ca              6.0000 H              10.0000 O
      2.0000 Si
****
     5 species in aqueous dissociation reaction:
     -1.0000  Afwillite                  -6.0000  H+
      2.0000  SiO2(aq)                    3.0000  Ca++
      6.0000  H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
        64.9272   60.0452   54.1005   48.5737
        43.1233   38.8084   35.2408   32.1136
*
*    gflag = 1 [reported delG0f]
*    extrapolation algorithm: Cp integration
*    ref-state data  [source: 82sar/bar]
*        delG0f = -1052.950 kcal/mol      [reported]
*        delH0f = -1143.200 kcal/mol      [reported]
*        delH0f = -1143.307 kcal/mol      [calculated]
*        S0PrTr =     74.600 cal/(mol*K)  [reported]
*    Cp coefficients [source: 77bar/kna   units: cal]
*        T**0   =  0.81540000E+02
*        T**1   =  0.45100000E-01
*        T**-2  = -0.14670000E+07
*        Tlimit =  626.85C
+----------------------------------------------------------------
Ca4Al2O7:13H2O
     sp.type =  solid
*    EQ3/6   =  com, alt, pit
     revised =  27-may-1988
*    mol.wt. =   560.470 g/mol
     V0PrTr  =   269.200 cm**3/mol [source: 78don    ]
****
     4 element(s):
      2.0000 Al              4.0000 Ca             26.0000 H
     20.0000 O
****
     5 species in aqueous dissociation reaction:
     -1.0000  Ca4Al2O7:13H2O            -14.0000  H+
      2.0000  Al+++                       4.0000  Ca++
     20.0000  H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
        500.0000  105.5443  500.0000  500.0000
        500.0000  500.0000  500.0000  500.0000
*
```

```
*     gflag = 1 [reported delG0f]
*     ref-state data  [source: 82sar/bar]
*         delG0f =  -1749.000 kcal/mol     [reported]
*         delH0f =      N/A
*         S0PrTr =      N/A
+-------------------------------------------------------------------
Ca4Al2O7:19H2O
      sp.type =  solid
*     EQ3/6   =  com, alt, pit
      revised =  27-may-1988
*     mol.wt. =   668.561 g/mol
      V0PrTr  =   370.910 cm**3/mol [source: 73don    ]
****
      4 element(s):
       2.0000 Al            4.0000 Ca             38.0000 H
      26.0000 O
****
      5 species in aqueous dissociation reaction:
      -1.0000  Ca4Al2O7:19H2O             -14.0000  H+
       2.0000  Al+++                        4.0000  Ca++
      26.0000  H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
       500.0000  101.9718  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
*
*     gflag = 1 [reported delG0f]
*     ref-state data  [source: 82sar/bar]
*         delG0f =  -2094.000 kcal/mol     [reported]
*         delH0f =      N/A
*         S0PrTr =      N/A
+-------------------------------------------------------------------
CaAl2O4:10H2O
      sp.type =  solid
*     EQ3/6   =  com, alt, pit
      revised =  27-may-1988
*     mol.wt. =   338.191 g/mol
      V0PrTr  =     0.000 cm**3/mol [source:         ]
****
      4 element(s):
       2.0000 Al            1.0000 Ca             20.0000 H
      14.0000 O
****
      5 species in aqueous dissociation reaction:
      -1.0000  CaAl2O4:10H2O              -8.0000  H+
       1.0000  Ca++                         2.0000  Al+++
      14.0000  H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
       500.0000   36.2852  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
*
*     gflag = 1 [reported delG0f]
*     ref-state data  [source: 82sar/bar]
*         delG0f =  -1107.000 kcal/mol     [reported]
*         delH0f =      N/A
*         S0PrTr =      N/A
+-------------------------------------------------------------------
Ca2Al2O5:8H2O
      sp.type =  solid
*     EQ3/6   =  com, alt, pit
      revised =  27-may-1988
*     mol.wt. =   358.238 g/mol
      V0PrTr  =   210.730 cm**3/mol [source: 73don    ]
```

```
****
     4 element(s):
      2.0000 Al               2.0000 Ca               16.0000 H
     13.0000 O
****
     5 species in aqueous dissociation reaction:
    -1.0000  Ca2Al2O5:8H2O                -10.0000  H+
     2.0000  Al+++                          2.0000  Ca++
    13.0000  H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
       500.0000   57.8593  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
*
*    gflag = 1 [reported delG0f]
*    ref-state data  [source: 82sar/bar]
*        delG0f = -1153.000 kcal/mol     [reported]
*        delH0f =      N/A
*        S0PrTr =      N/A
+------------------------------------------------------------------
Ettringite               Ca6Al2(SO4)3(OH)12:26H2O
     sp.type =  solid
*    EQ3/6   = com, alt, pit
     revised = 27-may-1988
*    mol.wt. = 1255.107 g/mol
     V0PrTr  =     0.000 cm**3/mol [source:          ]
****
     5 element(s):
      2.0000 Al               6.0000 Ca               64.0000 H
     50.0000 O                3.0000 S
****
     6 species in aqueous dissociation reaction:
    -1.0000  Ettringite                   -12.0000  H+
     2.0000  Al+++                          3.0000  SO4--
     6.0000  Ca++                          38.0000  H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
        66.8870   60.8127   54.7045   50.2795
        47.1404   45.4262  500.0000  500.0000
*
*    gflag = 2 [calculated delG0f(delH0f,S0PrTr)]
*    extrapolation algorithm: constant enthalpy approximation
*    ref-state data  [source: 82sar/bar]
*        delG0f = -3628.433 kcal/mol     [calculated]
*        delH0f = -4193.000 kcal/mol     [reported]
*        S0PrTr =   427.800 cal/(mol*K)  [reported]
+------------------------------------------------------------------
Gyrolite                 Ca2Si3O7(OH)2:1.5H2O
     sp.type =  solid    idealized
*    EQ3/6   = com, alt
     revised = 03-may-1990
*    mol.wt. =   337.446 g/mol
     V0PrTr  =   136.850 cm**3/mol [source: 74rob/rap]
****
     4 element(s):
      2.0000 Ca               5.0000 H               10.5000 O
      3.0000 Si
****
     5 species in aqueous dissociation reaction:
    -1.0000  Gyrolite                      -4.0000  H+
     2.0000  Ca++                           3.0000  SiO2(aq)
     4.5000  H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
```

```
        23.9501    22.9099    21.1748    19.4042
        17.6286    16.2361    15.0837    14.0228
*
*    gflag = 1 [reported delG0f]
*    extrapolation algorithm: Cp integration
*    ref-state data  [source: 82sar/bar]
*        delG0f =  -1085.650 kcal/mol      [reported]
*        delH0f =  -1175.850 kcal/mol      [reported]
*        delH0f =  -1176.542 kcal/mol      [calculated]
*        S0PrTr =      64.000 cal/(mol*K)  [reported]
*    Cp coefficients [source: 77bar/kna   units: cal]
*        T**0   =  0.79470000E+02
*        T**1   =  0.36300000E-01
*        T**-2  = -0.17550000E+07
*        Tlimit =  726.85C
+-------------------------------------------------------------------
Foshagite              Ca4Si3O9(OH)2:0.5H2O
    sp.type =  solid   idealized
*    EQ3/6   = com, alt
    revised = 03-may-1990
*    mol.wt. =   431.585 g/mol
    V0PrTr  =   154.230 cm**3/mol [source: 86jen    ]
****
    4 element(s):
     4.0000 Ca              3.0000 H              11.5000 O
     3.0000 Si
****
    5 species in aqueous dissociation reaction:
    -1.0000  Foshagite                 -8.0000  H+
    3.0000  SiO2(aq)                    4.0000  Ca++
    5.5000  H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
        71.3882    65.9210    59.0762    52.6162
        46.1816    41.0429    36.7540    32.9460
*
*    gflag = 1 [reported delG0f]
*    extrapolation algorithm: Cp integration
*    ref-state data  [source: 82sar/bar]
*        delG0f =  -1347.900 kcal/mol      [reported]
*        delH0f =  -1438.259 kcal/mol      [reported]
*        S0PrTr =      78.950 cal/(mol*K)  [reported]
*    Cp coefficients [source: 77bar/kna   units: cal]
*        T**0   =  0.87950000E+02
*        T**1   =  0.39500000E-01
*        T**-2  = -0.13480000E+07
*        Tlimit =  726.85C
+-------------------------------------------------------------------
Gypsum                 CaSO4:2H2O
    sp.type =  solid
*    EQ3/6   = com, alt, pit
    revised = 18-may-1990
*    mol.wt. =   172.172 g/mol
    V0PrTr  =    74.690 cm**3/mol [source:          ]
****
    4 element(s):
     1.0000 Ca              4.0000 H               6.0000 O
     1.0000 S
****
    4 species in aqueous dissociation reaction:
    -1.0000  Gypsum                     1.0000  Ca++
    1.0000  SO4--                       2.0000  H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
```

```
           -4.5331    -4.4823    -4.6094    -4.9035
           -5.4299    -6.1266    -7.0386    -8.3003
*
*    gflag = 1 [reported delG0f]
*    extrapolation algorithm: Cp integration
*    ref-state data  [source: 79rob/hem]
*        delG0f =  -1797.197 kj/mol         [reported]
*        delH0f =  -2022.628 kj/mol         [reported]
*        delH0f =  -2022.683 kj/mol         [calculated]
*        S0PrTr =    194.140 j/(mol*K)      [reported]
*    Cp coefficients [source: 77bar/kna    units: cal]
*        T**0  =  0.21840000E+02
*        T**1  =  0.76000000E-01
*        Tlimit = 526.85C
+----------------------------------------------------------------
Hillebrandite           Ca2SiO3(OH)2:0.17H2O
     sp.type =  solid   idealized
*    EQ3/6   =  com, alt
     revised =  14-may-1990
*    mol.wt. =  193.317 g/mol
     V0PrTr  =    71.790 cm**3/mol [source: 86jen    ]
****
     4 element(s):
      2.0000 Ca              2.3400 H              5.1700 O
      1.0000 Si
****
     5 species in aqueous dissociation reaction:
     -1.0000  Hillebrandite             -4.0000  H+
      1.0000  SiO2(aq)                   2.0000  Ca++
      3.1700  H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
        39.9804    36.8190    33.0171    29.4948
        26.0166    23.2516    20.9531    18.9281
*
*    gflag = 1 [reported delG0f]
*    extrapolation algorithm: Cp integration
*    ref-state data  [source: 82sar/bar]
*        delG0f =   -592.900 kcal/mol      [reported]
*        delH0f =   -637.150 kcal/mol      [reported]
*        delH0f =   -637.402 kcal/mol      [calculated]
*        S0PrTr =     38.400 cal/(mol*K)   [reported]
*    Cp coefficients [source: 77bar/kna    units: cal]
*        T**0  =  0.41040000E+02
*        T**1  =  0.22400000E-01
*        T**-2 = -0.74000000E+06
*        Tlimit = 626.85C
+----------------------------------------------------------------
Monohydrocalcite        CaCO3:H2O
     sp.type =  solid
*    EQ3/6   =  com, alt
     revised =  01-feb-1983
*    mol.wt. =  118.102 g/mol
     V0PrTr  =    48.700 cm**3/mol [source:           ]
****
     4 element(s):
      1.0000 C               1.0000 Ca             2.0000 H
      4.0000 O
****
     5 species in aqueous dissociation reaction:
     -1.0000  Monohydrocalcite          -1.0000  H+
      1.0000  Ca++                       1.0000  H2O
      1.0000  HCO3-
*
```

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```
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
        3.0112    2.6824    2.3085    1.9822
        1.6621    1.3727  500.0000  500.0000
*
*    gflag = 1 [reported delG0f]
*    extrapolation algorithm: constant enthalpy approximation
*    ref-state data  [source: 79rob/hem]
*        delG0f =  -1361.600 kj/mol        [reported]
*        delH0f =  -1498.290 kj/mol        [reported]
*        S0PrTr =    129.827 j/(mol*K)     [reported]
+------------------------------------------------------------------
Okenite                CaSi2O4(OH)2:H2O
     sp.type =  solid    idealized
*    EQ3/6   = com, alt
     revised =  27-may-1988
*    mol.wt. =   212.277 g/mol
     V0PrTr  =    94.770 cm**3/mol [source: 86jen    ]
****
     4 element(s):
      1.0000 Ca              4.0000 H              7.0000 O
      2.0000 Si
****
     5 species in aqueous dissociation reaction:
     -1.0000  Okenite                    -2.0000  H+
      1.0000  Ca++                        2.0000  SiO2(aq)
      3.0000  H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
       10.5447   10.3816    9.9482    9.5671
        9.3465    9.3477  500.0000  500.0000
*
*    gflag = 1 [reported delG0f]
*    extrapolation algorithm: constant enthalpy approximation
*    ref-state data  [source: 82sar/bar]
*        delG0f =   -686.400 kcal/mol     [reported]
*        delH0f =   -749.638 kcal/mol     [reported]
*        S0PrTr =     40.900 cal/(mol*K)  [reported]
+------------------------------------------------------------------
Portlandite            Ca(OH)2
     sp.type =  solid
*    EQ3/6   = com, alt, pit
     revised =  17-may-1990
*    mol.wt. =    74.093 g/mol
     V0PrTr  =    33.056 cm**3/mol [source:          ]
****
     3 element(s):
      1.0000 Ca              2.0000 H              2.0000 O
****
     4 species in aqueous dissociation reaction:
     -1.0000  Portlandite                -2.0000  H+
      1.0000  Ca++                        2.0000  H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
       24.6242   22.5552   20.1960   18.0608
       15.9702   14.3128   12.9403   11.7465
*
*    gflag = 1 [reported delG0f]
*    extrapolation algorithm: Cp integration
*    ref-state data  [source: 79rob/hem]
*        delG0f =   -898.408 kj/mol        [reported]
*        delH0f =   -986.070 kj/mol        [reported]
*        S0PrTr =     83.390 j/(mol*K)     [reported]
*    Cp coefficients [source: 79rob/hem   units: jou]
*        T**0  = 0.18667000E+03
```

```
*        T**1   = -0.21911000E-01
*        T**-.5 = -0.15998000E+04
*        Tlimit =  426.85C
+-------------------------------------------------------------------
Tobermorite-11A          Ca5Si6H11O22.5
     sp.type =  solid    idealized
*    EQ3/6   =  com, alt
     revised =  18-may-1990
*    mol.wt. =   739.977 g/mol
     V0PrTr  =   286.810 cm**3/mol [source: 86jen    ]
****
     4 element(s):
      5.0000 Ca            11.0000 H              22.5000 O
      6.0000 Si
****
     5 species in aqueous dissociation reaction:
     -1.0000  Tobermorite-11A            -10.0000  H+
      5.0000  Ca++                         6.0000  SiO2(aq)
     10.5000  H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
         69.6267   65.6121   59.9062   54.3181
         48.7422   44.3339   40.6665   37.3382
*
*    gflag = 1 [reported delG0f]
*    extrapolation algorithm: Cp integration
*    ref-state data  [source: 82sar/bar]
*        delG0f = -2361.450 kcal/mol     [reported]
*        delH0f = -2556.300 kcal/mol     [reported]
*        delH0f = -2556.407 kcal/mol     [calculated]
*        S0PrTr =    146.150 cal/(mol*K) [reported]
*    Cp coefficients [source: 73bar/kna   units: cal]
*        T**0  = 0.11060000E+03
*        T**1  = 0.18910000E+00
*        Tlimit = 726.85C
+-------------------------------------------------------------------
Tobermorite-14A          Ca5Si6H21O27.5
     sp.type =  solid    idealized
*    EQ3/6   =  com, alt
     revised =  18-may-1990
*    mol.wt. =   830.053 g/mol
     V0PrTr  =     0.000 cm**3/mol [source:          ]
****
     4 element(s):
      5.0000 Ca            21.0000 H              27.5000 O
      6.0000 Si
****
     5 species in aqueous dissociation reaction:
     -1.0000  Tobermorite-14A            -10.0000  H+
      5.0000  Ca++                         6.0000  SiO2(aq)
     15.5000  H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
         67.0302   63.8445   59.2602   54.8933
         50.7382   47.6367   45.1577   42.8940
*
*    gflag = 1 [reported delG0f]
*    extrapolation algorithm: Cp integration
*    ref-state data  [source: 82sar/bar]
*        delG0f = -2647.300 kcal/mol     [reported]
*        delH0f = -2911.250 kcal/mol     [reported]
*        delH0f = -2911.351 kcal/mol     [calculated]
*        S0PrTr =    193.150 cal/(mol*K) [reported]
*    Cp coefficients [source: 73bar/kna   units: cal]
```

```
*          T**0   =  0.13220000E+03
*          T**1   =  0.17000000E+00
*          Tlimit =  726.85C
+-------------------------------------------------------------------
Tobermorite-9A          Ca5Si6H6O20
     sp.type =  solid    idealized
*    EQ3/6   =  com, alt
     revised =  18-may-1990
*    mol.wt. =   694.939 g/mol
     V0PrTr  =     0.000 cm**3/mol [source:          ]
****
     4 element(s):
      5.0000 Ca              6.0000 H              20.0000 O
      6.0000 Si
****
     5 species in aqueous dissociation reaction:
     -1.0000  Tobermorite-9A          -10.0000  H+
      5.0000  Ca++                      6.0000  SiO2(aq)
      8.0000  H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
        73.7598   69.0798   62.5628   56.1789
        49.7451   44.5892   40.2473   36.2869
*
*    gflag = 1 [reported delG0f]
*    extrapolation algorithm: Cp integration
*    ref-state data   [source: 82sar/bar]
*        delG0f =  -2215.000 kcal/mol     [reported]
*        delH0f =  -2375.000 kcal/mol     [reported]
*        delH0f =  -2375.410 kcal/mol     [calculated]
*        S0PrTr =    122.650 cal/(mol*K)  [reported]
*    Cp coefficients [source: 73bar/kna   units: cal]
*        T**0   =  0.14355000E+03
*        T**1   =  0.74700000E-01
*        T**-2  = -0.20820000E+07
*        Tlimit =  726.85C
+-------------------------------------------------------------------
Xonotlite               Ca6Si6O17(OH)2
     sp.type =  solid
*    EQ3/6   =  com, alt
     revised =  03-apr-1990
*    mol.wt. =   714.985 g/mol
     V0PrTr  =   264.810 cm**3/mol [source: 86jen    ]
****
     4 element(s):
      6.0000 Ca              2.0000 H              19.0000 O
      6.0000 Si
****
     5 species in aqueous dissociation reaction:
     -1.0000  Xonotlite               -12.0000  H+
      6.0000  Ca++                      6.0000  SiO2(aq)
      7.0000  H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
        99.2625   91.8267   82.4135   73.7131
        65.4107   59.1548  500.0000  500.0000
*
*    gflag = 1 [reported delG0f]
*    extrapolation algorithm: constant enthalpy approximation
*    ref-state data   [source: 82sar/bar]
*        delG0f =  -2259.400 kcal/mol     [reported]
*        delH0f =  -2396.700 kcal/mol     [reported]
*        delH0f =  -2397.242 kcal/mol     [calculated]
*        S0PrTr =    121.300 cal/(mol*K)  [reported]
```

```
+-------------------------------------------------------------------
Wollastonite          CaSiO3
     sp.type =  solid
*    EQ3/6   =  com, alt, sup
     revised =  08-aug-1984
*    mol.wt. =   116.162 g/mol
     V0PrTr  =    39.930 cm**3/mol [source: supcrt92 [see 92joh/oel]]
****
     3 element(s):
      1.0000 Ca             3.0000 O             1.0000 Si
****
     5 species in aqueous dissociation reaction:
     -1.0000  Wollastonite              -2.0000  H+
      1.0000  Ca++                       1.0000  H2O
      1.0000  SiO2(aq)
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
         14.8822    13.7605    12.2730    10.8315
          9.3747     8.1989     7.2075     6.3148
*
*    gflag = 1 [reported delG0f]
*    extrapolation algorithm: supcrt92 [92joh/oel]
*    ref-state data  [source: supcrt92 [see 92joh/oel]]
*        delG0f =   -369.225 kcal/mol     [reported]
*        delH0f =   -389.590 kcal/mol     [reported]
*        S0PrTr =     19.600 cal/(mol*K)  [reported]
*    Cp coefficients [source: supcrt92 [see 92joh/oel]]
*        T**0   =  0.26640000E+02
*        T**1   =  0.36000000E-02
*        T**-2  = -0.65200000E+06
*        Tlimit = 1126.85C
+-------------------------------------------------------------------
```