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Solubility behavior of Ca-, S-, Al-, and Si-bearing solid phases in Portland cement pore solutions as a function of hydration time

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Abstract

The concentrations of Ca, S, Al, Si, Na, and K in the pore solutions of ordinary Portland cement (OPC) and white Portland cement (WPC) pastes were measured during the first 28 days of hydration at room temperature. Saturation indices (SI) with respect to various solid phases known to occur in cement pastes were calculated from a thermodynamic analysis of the elemental concentrations, resulting in good agreement between the two pastes. In agreement with other published work, gypsum was saturated during the first several hours of hydration and then undersaturated thereafter, while portlandite was modestly supersaturated after the first few hours. High levels of supersaturation with respect to ettringite and calcium monosulfoaluminate were calculated, particularly prior to the consumption of gypsum at around 10 h. Results are consistent with published thermodynamic studies that show calcium monosulfoaluminate is metastable with respect to ettringite under normal hydration conditions. Three different ion activity product (IAP) equations for C-S-H were applied to the data. From 10 h onward, each of the IAP values declined gradually over time and the values for the OPC and WPC pastes were in close agreement. The same IAP equations were applied to experimental data from the pure CaO $-SiO_2-H_2O$ system, resulting in good agreement between the cement paste pore solutions and the equilibrium between portlandite and the upper, or metastable, C-S-H solubility curve.

Keywords: Pore solution; Thermodynamic calculations; Hydration; Hydration products; C-S-H

1. Introduction

The composition of the aqueous phase has long been used to infer information about the solid phases present in Portland cement pastes and their level of saturation at various hydration times [1-7]. Most of these studies report the concentrations of calcium, sodium, potassium, and sulfur, all of which occur in millimolar concentrations in the pore solution, allowing the solubility behavior of portlandite (CH¹) and gypsum (CSH₂) to be studied. However, few data exist for aluminum and silicon, as these elements occur at micromolar concentrations in the pore solution and are difficult to measure accurately. Conse-

quently, important questions remain regarding the solubility behavior of phases that contain these components during the hydration of Portland cement. For example, no studies have addressed relative saturation levels of the calcium sulfoaluminate phases ettringite ($C_6A\bar{S}_3H_{32}$) and calcium monosulfoaluminate ($C_4A\bar{S}H_{12}$), an issue that has important implications for durability. Also, it remains unclear how the solubility of the C-S-H gel produced by the hydration of Portland cement, which is a relatively complex multicomponent system, relates to the solubility of the various types of C-S-H that can be produced within the pure CaO-SiO₂-H₂O system, for example, by the hydration of pure C_3S or C_2S minerals or by precipitation from aqueous suspensions [6,8]. In this paper, the concentrations of Ca, Na, K, Al, S, and Si in the pore solutions of hardened cement pastes are reported together for the first time, allowing these issues to be addressed.

Portland cements contain appreciable amounts of highly soluble alkali compounds. As a result, the pH and ionic strength of the pore solution remain high at all times. This

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 $^{^1}$ Cement chemistry notation: C=CaO, S=SiO_2, A=Al_2O_3, N=Na_2O, K=K_2O, \bar{S}=SO_3, and H=H_2O.

means that the composition of the solution in which minerals are in equilibrium is very different from the final conditions after the mineral is dissolved in pure water, which can affect the solubility behavior [9,10]. Alkalis in the pore solution also create common ion effects that can cause large variations in the concentrations of individual elements from one paste to another. Accounting for these effects requires measuring the concentrations of all components occurring at micromolar or greater levels in the pore solution even when only a particular subset of elements is of interest. The effects of pH and ionic strength on the solubility behavior were explored in this study by using two cements with significantly different alkali contents and by using a lower water-to-cement ratio (w/c) for the higher alkali cement.

Solubility relationships in Portland cement pastes are modeled using pore solution data collected from the start of hydration through approximately 28 days. After using a thermodynamic analysis to speciate the pore fluid, saturation levels in the C-N-K-A- \bar{S} -H system are analyzed by calculating the ion activity products (IAPs) of portlandite, gypsum, monosulfate, and ettringite and dividing by the equilibrium solubility product. The analysis then shifts to the C-S-H gel, which is more complex because it has a variable composition and dissolves incongruently. For the C-S-H gel, three different IAP equations are applied to the data to investigate the solubility behavior. As a comparison, the same thermodynamic analysis is also applied to apparent invariant points in the pure CaO-SiO₂-H₂O system.

2. Experimental

Neat cement pastes with w/c of 0.35 and 0.50 were prepared using a Type I ordinary Portland cement (OPC) and a Type I white Portland cement (WPC), respectively. Table 1 gives the compositions of the cements. Cement powder was added to deionized water and mixed for 5 min in a planetary-type mixer, and then the pastes were cast into 5×18 cm plastic compression cylinders to give approximately 300-g samples. The cylinders were sealed and stored at room temperature (~22 °C) until extraction of the pore fluid.

The collection of pore fluids prior to set was by vacuum filtration using 0.22- μ m filter paper in a glove box with flowing nitrogen. Storage of the pore fluids in sealed 30-ml plastic vials until analysis further minimized potential carbonation effects. After set, pore fluids were extracted using the steel die press method, following the protocol outlined by Barneyback and Diamond [11]. Samples were demolded, crushed, and loaded into the apparatus, which was constructed using the same materials (ASTM 4340 steel) and specifications described in Ref. [11]. The application of ~550-MPa pressures to ~250-g samples provided sufficient volumes of pore fluid within 15–30 min after the initial application of pressure. The collection of the pore fluid with

Table 1	
Compositional data	for OPC and WPC

	OPC	WPC
Element (wt.%)		
CaO	63.22	68.34
SiO ₂	20.80	24.30
Al ₂ O ₃	4.62	1.94
Fe ₂ O ₃	2.57	0.37
MgO	4.15	0.59
Na ₂ O	0.16	0.13
K ₂ O	0.51	0.02
SO ₃	2.70	2.01
Bogue mineralogy (wt.%)		
C ₃ S	58	72
C_2S	16	17
C ₃ A	7	5
C ₄ AF	12	1
Other		
Free lime (wt.%)	0.41	1.57
LOI (wt.%)	0.90	1.58
Blaine surface area (m ² /kg)	312	446

10-ml plastic syringes and their subsequent transfer to 30-ml plastic vials minimized contact of the fluids with CO_2 . Analysis of the samples by inductively coupled plasma atomic emission spectrometry, performed with appropriate ionic standards within hours of the extraction, provided the elemental concentration data.

3. Results—elemental concentrations

Table 2 lists the measured elemental concentrations in the pore solutions. The duration and timing of pore solution extractions differed for the two types of paste, but both data sets start within 1 h of mixing and extend to at least 568 h. The elemental concentrations often differ between the two pastes by more than an order of magnitude at a given time. Alkali concentrations (Na and K) increased significantly during the first few days, reflecting the decreasing amount of liquid water, and then stabilized. Large and rapid changes in the concentrations of calcium, sulfur, aluminum, and silicon occurred between about 6 and 12 h in pore solutions from both pastes. These changes are caused by the consumption of the gypsum (present as an additive to the cements) through reaction with C₃A. For purposes of discussion, we divide the hydration into two stages based on this change: Stage A, from 0 to 12 h and Stage B, from 12 h onward. During Stage B, the aluminum and silicon concentrations in the OPC paste increase steadily, while in the WPC paste the aluminum concentration decreases slightly and the silicon concentration is unchanged. However, these differences in behavior are not reflected in the calculated saturation levels, which are discussed in Section 5.

The concentration trends in calcium and sulfur reported here are consistent with previous studies [1,2,12]. The data

Table 2Elemental concentrations for OPC and WPC

Time (h)	Na (mM)	K (mM)	S (mM)	Si (µM)	Al (µM)	Ca (mM)	Na and K (mM)
OPC (w/c = 0.	35)						
0.5	65.2	273.2	149.0	95	117	15.5	338.4
2	70.8	283.6	142.9	72	120	15.4	354.4
3	69.1	277.2	144.9	73	117	15.0	346.3
4	78.6	298.9	156.7	62	133	18.4	377.5
6	81.8	303.5	163.8	62	139	18.0	385.3
12	102.1	298.9	36.2	218	61	3.3	401.0
20	102.0	299.6	32.7	221	64	3.0	401.6
24	99.1	289.5	18.4	234	117	2.7	388.6
43	117.0	301.2	11.8	240	139	2.1	418.2
73	122.2	287.4	9.6	280	194	1.9	409.6
93	124.0	310.1	8.9	254	194	2.0	434.1
121	128.9	327.5	9.9	228	178	1.7	456.4
140	140.4	309.4	9.7	291	239	1.8	449.8
170	124.7	270.9	9.9	246	205	1.8	395.6
184	115.9	225.1	8.3	261	194	1.9	341.0
476	124.0	237.9	12.3	340	233	1.9	361.9
569	125.8	237.3	13.0	350	261	1.8	363.1
WPC (w/c = 0.	.50)						
0.1	6.0	1.9	24.2	39	130	45.3	7.9
3	9.0	2.6	14.0	46	125	42.0	11.6
6	10.8	2.9	12.1	56	120	36.9	13.7
10	29.4	4.8	4.1	19	98	26.1	34.2
18	48.3	8.0	0.2	24	78	16.8	56.3
28	50.1	6.1	0.1	29	75	14.2	56.2
66	55.8	7.3	0.2	31	74	11.6	63.1
168	57.8	7.9	0.1	28	71	11.9	65.7
336	62.4	8.5	0.1	24	63	9.2	70.9
672	65.7	9.3	0.1	24	69	10.1	75.0

also illustrate common ion effects similar to those documented in the C-N-K- \overline{S} -H [13] and the C-N-K-H systems [14]. The concentrations of calcium and sulfur in the OPC and WPC pore solutions during Stage A are similar to equilibrium concentrations calculated for alkaline solutions saturated with gypsum and CH (see Fig. 1), while in Stage B



Fig. 1. Calcium and sulfur concentrations during Stage A plotted as a function of alkali content, illustrating common ion effects. The solid lines are the calculated Ca and S concentrations for the equilibrium between portlandite and gypsum.

the calcium concentrations are similar to equilibrium concentrations calculated for alkaline solutions saturated with respect to only CH. Further insight into the solubility of solid phases in the pore solutions requires thermodynamic analysis of the data.

4. Thermodynamic modeling

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Thermodynamic modeling of saturation levels requires the assumption of local equilibrium, where rates of dissolution/precipitation are much faster than rates of ionic transport, so that mineral solubilities control the chemistry of the aqueous phase. Determining the thermodynamic activity of the aqueous species for the relevant equilibria in the system of interest is the first step toward modeling saturation levels in such systems. The relationship that defines the activity of each species (a_i) is given in Eq. (1)

$$a_1 = m_i \gamma_i \tag{1}$$

where γ_i is the activity coefficient and m_i is the molality of each species, *i*. The elemental concentrations reported in Table 2 were converted to molality for the calculations described in this section.

For solutions with ionic strengths greater than 0.1 but less than 0.5, activity coefficients can be calculated using one of several extensions of the Debye–Hückel equation. The expression for calculating the ionic strength, I, of a solution is given in Eq. (2):

$$I = \frac{1}{2} \sum_{i} z_i^2 m_i \tag{2}$$

where z_i is the unit charge of species *i*, m_i is the molality of species *i*, and the summation is for all charged ionic species in the solution. In this study, the WATEQ [10] extended Debye-Hückel equations were used for ionic species for which the ionic size parameters were available and the standard Davies equation was used for all other ions. Calculating activities for neutral ion pairs required a different approach. In theory, a neutral ion should be unaffected by the charged ions in solution and thus have unit activity at moderate ionic strengths. However, ionic associates form dipoles, causing them to interact with charged species. The calculations presented here use the empirically determined Debye-Hückel parameters proposed by Reardon and Langmuir [15] for the neutral dipoles CaSO4° and NaOH°, and their NaOH° value is also assigned to KOH°. Table 3 lists the formulations of the equations used to calculate the activity coefficients and the values of the parameters used for each ion.

Table 4 lists the IAP equations and the equilibrium solubility products (K_{sp}) at 25 °C of the ionic species and

Table 3

Thermodynamic	data	for	activity	coefficient	calculations
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Species	Debye-Hückel a	Debye-Hückel b
Ca ²⁺	5	0.165
$CaSO_4^\circ$	_	-0.45
H^+	9	0
K ⁺	4	0.075
KOH°	_	-0.10
Na ⁺	4	0.075
NaOH°	_	-0.10
SO_{4}^{2} -	5	-0.04
$Al(OH)_4^-$	Davies equation	
CaOH ⁺	Davies equation	
KSO_4^-	Davies equation	
NaSO ₄	Davies equation	
$H_4SiO_4^\circ$	Davies equation	
$H_3SiO_4^-$	Davies equation	
H ₂ SiO ₄ ²⁻	Davies equation	

Davies equation:

$$\log \gamma_i = -Az_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right).$$

WATEQ extended Debye-Hückel equation:

$$\log \gamma_i = \frac{-Az_i^2 \sqrt{I}}{1 + Ba_i \sqrt{I}} + b_i I.$$

A and B are Debye-Hückel solvent parameters dependent only on temperature, a_i is the Debye-Hückel ion-size parameter, and b_i is the WATEQ Debye-Hückel parameter.

Table 4 Thermodynamic data for solubility calculations at 25 $^\circ \rm C$

Mineral or species	Reaction	$\log K_{\rm sp}$
CaOH ⁺	$Ca^{2+} + OH^{-} \rightarrow CaOH^{+}$	1.18
CaSO ₄	$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4^{\circ}$	2.11
NaOH°	$Na^+ + OH^- \rightarrow NaOH^\circ$	-0.21
$NaSO_4^-$	$Na^+ + SO_4^{2-} \rightarrow NaSO_4^-$	0.70
KOH°	$K^+ + OH^- \rightarrow KOH^\circ$	-0.46
KSO_4^-	$\mathrm{K^{+}} + \mathrm{SO_{4}^{2-}} \rightarrow \mathrm{KSO_{4}^{-}}$	0.85
$H_3SiO_4^-$	$H_4SiO_4^{\circ} \rightarrow H_3SiO_4^{-} + H^+$	- 9.83
$H_2SiO_4^2$ –	$H_4SiO_4^\circ \rightarrow H_2SiO_4^{2-} + 2H^+$	-23.00
Portlandite	$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$	-5.20
Gypsum	$CaSO_4 \cdot 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$	-4.58
Monosulfate	$3CaO(Al_2O_3) \cdot (CaSO_4) \cdot 12(H_2O) \rightarrow 4Ca^{2+} +$	- 29.43
	$2AI(OH)_{4}^{-} + SO_{4}^{2-} + 4OH^{-} + 6H_{2}O$	
Ettringite	$Ca_{6}Al_{2}(SO_{4})_{3}(OH^{-})_{12}(H_{2}O)_{26} \rightarrow 6Ca^{2+} +$	-45.00
-	$2\text{Al}(\text{OH})_4^- + 3\text{SO}_4^2^- + 4\text{OH}^- + 26\text{H}_2\text{O}$	

solid phases considered in the calculations. All calculations were carried out at 22 °C, so the standard 25 °C log K_{sp} values were modified slightly using the enthalpy of formation for the ions. The values shown in Table 4 were taken from the PHREEQC thermodynamic database of Parkhurst [16], with the following exceptions. The value for ettringite reflects the 25 °C log K_{sp} value of -45.0 reported by both Perkins and Palmer [17] and Warren and Reardon [18]. The log K_{sp} value for monosulfate reflects the 25 °C value reported by Damidot and Glasser [19].

The calculation of saturation indices (SI) follows from

$$SI = \log \frac{IAP}{K_{sp}}.$$
(3)

The form of Eq. (3) dictates that SI=0 indicates saturation, SI>0 indicates supersaturation, and SI<0 indicates undersaturation.

Determining the activities of all the ionic species in solution requires iterative calculations. This work used the geochemical modeling program PHREEQC [16] with a thermodynamic database modified for cementitious systems. These calculations adjusted the hydroxyl concentration to maintain electroneutrality in the solutions, such that the reported pH values are calculated, rather than measured, values. The results of the speciation and SI calculations for one pore solution composition are given in Table 5.

The results of calculations of the ionic strength and pH at different times for each pore solution are shown in Fig. 2. The ionic strength in the OPC paste reached a maximum value of about 0.45 near the end of Stage A and never fell below 0.3. The ionic strength of the WPC paste was close to 0.1 throughout the hydration. The pH of the OPC paste increased sharply from about 12.8 to 13.4 from Stage A to Stage B and remained fairly steady thereafter. The pH of the WPC solution underwent a more modest increase, reaching a maximum value of about 12.8 at the end of the experiment. The higher ionic strength and the higher pH in the OPC pore solutions both result from the higher concentra-

Resul	esults of a thermodynamic calculation: OPC paste at 12 h ^a													
Ionic strength = 0.40, pH = 13.41														
	Ca ²⁺	CaSO_4°	CaOH ⁺	\mathbf{K}^+	KSO ₄ ^{2 –}	KOH°	Na ⁺	$NaSO_4^-$	NaOH°	Al(OH) ₄	SO_4^{2-}	$\mathrm{H_2SiO_4^{2-}}$	${\rm H_3SiO_4^-}$	$H_4SiO_4^\circ$
$\ln(a)$	- 3.42	- 3.59	- 2.97	-0.70	- 2.15	- 1.82	- 1.19	- 2.77	- 2.06	- 4.35	-2.27	-4.31	- 4.47	-8.00
			Portlandite				Gypsum			Ettringite				Monosulfate
SI			0.36				- 1.12			6.44				1.98

Table 5

^a For the elemental concentrations, see Table 2.

tion of alkalis in these solutions. The increase in pH at the Stage A/Stage B transition is a result of the decrease in sulfur concentration, which increases the demand for hydroxyl ions to maintain electroneutrality.

5. Results-solubility behavior

5.1. SI in the C-N-K-A- \overline{S} -H system

The phases in the C-N-K-A-S-H system that are normally found in cement pastes are portlandite, gypsum, calcium monosulfoaluminate ("monosulfate"), and ettringite. The IAP equations and K_{sp} values used for these phases are given in Table 4. Other phases that can occur under some conditions include hydrogarnet (C_3AH_6), syngenite (KCS₂H), thenardite-mirabilite ($N_2\bar{S}-N_2\bar{S}H_{10}$), epsomite (M $\bar{S}H_7$), and gibbsite (AH₃). However, calculations indicated undersaturation at all times with respect to the latter group of minerals so they are not discussed further.

Fig. 3a shows the SI for portlandite as a function of time. The SI for both pastes increased initially, reached a maximum supersaturation at about 10 h, and then decreased gradually thereafter, approaching saturation by the end of the 28-day experiment. Changes in the SI were more pronounced in the OPC pore solution, which was undersaturated during the first few hours and then increased sharply at the Stage A/Stage B transition. The OPC paste took slightly longer to reach portlandite saturation than was reported in Ref. [4]; the difference could be due to the differences in w/c ratio or cement fineness.



Fig. 2. Calculated values of the pH and ionic strength of the cement pastes.



Fig. 3. SI (see Eq. (3)) of (a) portlandite and (b) gypsum in the cement pastes as a function of hydration time. A value of zero indicates saturation.



Fig. 4. SI (see Eq. (3)) of (a) ettringite and (b) monosulfate in the cement pastes as a function of hydration time. A value of zero indicates saturation.

Fig. 3b shows the SI for gypsum. Both pastes are saturated with respect to gypsum in Stage A and undersaturated in Stage B. As noted earlier, the consumption of gypsum is the cause of the transition from Stage A to Stage B. Bailey and Hampson [3] observed a sharp decrease in the degree of gypsum supersaturation during the first several minutes of hydration, which they attributed to the conversion of anhydrite to gypsum. The current data sets do not cover such early times, although the WPC calculations indicate slight supersaturation at approximately 15 min.

The SI for monosulfate and ettringite are shown in Fig. 4a and b for the OPC and WPC pore solutions. Both solutions were supersaturated with respect to monosulfate and ettringite throughout the experiment. There was a sharp drop in the SI between Stage A and Stage B in both solutions. The very high levels of supersaturation during Stage A could be due to the formation of metastable aluminum compounds around the hydrating grains (see discussion in Ref. [6, p. 193]). It should also be noted that the SI values are magnified by the large stoichiometric coefficients in the IAP equations for these phases. The SI for ettringite are greater than those of monosulfate at all times, and thus there is no evidence in the present results of the conversion of ettringite into monosulfate that is generally observed to occur during the time frame studied. The present calculations are

consistent with other thermodynamic calculations that predict ettringite to be the stable calcium sulfoaluminate phase in Portland cement pastes under normal conditions (e.g., Ref. [20]).

5.2. C-S-H solubility behavior

Because there is no widely accepted IAP equation or associated equilibrium solubility product for the C-S-H gel that forms in cement paste, SI cannot be calculated directly. However, IAP equations for C-S-H can be generated based on various assumptions, and the changes in the value of an IAP with hydration time, and for different cement pastes, can be compared. A simple approach is to formulate an IAP from the most abundant ions, fixing the ratios to maintain charge balance. Assuming the C-S-H gel to have a C/S ratio of 1.7 and using the most abundant calcium and silicon ions in the pore solution result in:

$$IAP_{cb} = [Ca^{2+}]^{1.7} [H_2 SiO_4^{2-}] [OH^{-}]^{1.4}.$$
 (4)

This approach does not incorporate structural considerations or take into account other ions such as $CaOH^+$. The amount of bound water assigned to the gel by Eq. (4) is determined only from charge balance, but the result is quite compatible with measured values of C-S-H bound water [6].

Glasser et al. [21] incorporated available compositional and structural information to derive a composition for C-S-H that is a function of C/S ratio and CH content. They then used solubility data for C-S-H formed by precipitation from solutions with C/S ranging from 1.0 to 1.4 to derive associated IAP equations and equilibrium solubility products. The thermodynamic analysis does not extend to C/S>1.4, but, based on some reasonable assumptions and the compositional measurements of Sierra [22], the authors proposed an IAP appropriate for C-S-H gel as it occurs in cement paste:

$$\begin{split} IAP_{GI} &= (Ca^{2+})^{(3.5-y)/2} (CaOH^{+})^{y/2} \\ &\times (H_2 SiO_4^{2-}) (OH^{-})^{(3-y)/2} \end{split} \tag{5}$$

where y is the concentration of CaOH⁺ ions in the solution divided by the sum of the Ca²⁺ and CaOH⁺ concentrations. In Eq. (5), the C/S ratio is 1.75 and the H/S ratio varies with pH but is close to the value of 1.4 obtained in Eq. (4). Both Ca²⁺ and CaOH⁺ enter the C-S-H structure; while $H_2SiO_4^{2-}$ is the only silica species.

Another approach is to model the C-S-H gel as a nonideal, Margules-type binary solid solution that dissolves incongruently [23,24]. In this study, we used the IAP formulation of Kersten [24], who derived a model based on a generalized form of the Gibbs–Duhem equation and structural information on C-S-H:

$$IAP_{K} = [(CaOH^{+}) + (OH^{-})](H_{3}SiO_{4}^{-}).$$
(6)



Fig. 5. Calculated IAP_{C-S-H} values for the OPC and WPC pastes as a function of hydration time. (a) $log(IAP_{CB})$ as defined by Eq. (4). (b) $log(IAP_{GI})$ as defined by Eq. (5). (c) $log(IAP_K)$ as defined by Eq. (6).

Fig. 5 shows the *IAP* values calculated from Eqs. (4)-(6) as a function of time. The behavior for each IAP equation is similar. In each case, the IAP values for the WPC paste are higher in Stage A, but during the Stage A/Stage B transition the values for the two pastes converge and remain in good agreement thereafter. During Stage B the IAP values decline gradually, indicating either decreasing levels of supersaturation or a phase that is becoming less soluble with time due to structural changes. While the data presented in this work do not validate any one IAP_{C-S-H} formulation over another, the agreement in the IAP values for the OPC and WPC cement pastes in Stage B supports the hypothesis that the pore solutions are in a metastable equilibrium with C-S-H gel.

In the pure CaO–SiO₂–H₂O system, the Gibbs phase rule dictates that plots of the concentration of calcium and silica from solutions in contact with a single phase should yield a smooth curve if equilibrium holds. Jennings [8] plotted an array of C-S-H solubility data from the available literature on a semilogarithmic diagram and found that the points formed two curves, suggesting that thermodynamic equilibrium is attained with one or the other of two phases (see Fig. 6). Points on the upper curve (M in Fig. 6) were obtained from the hydration of C₃S in stirred suspensions, with longer hydration times leading to points farther to the right (higher Ca concentrations). Data points on the lower curve (S in Fig. 6) are primarily from C-S-H formed by precipitation from solutions, and for this curve the higher the C/S molar ratio of the C-S-H, the farther the points are to the right. Some experiments using C_3S gave data points on the lower curve after long hydration times. Curve S represents the solubility of C-S-H (I), a more crystalline analogue to the C-S-H found in cement paste [6]. The meaning of the upper curve is less well defined. It may represent the solubility of C-S-H formed as a surface layer on C_3S , or it may represent a level of supersaturation with respect to the lower curve (see discussion in Refs. [25,26]). There are very few data available from hardened C_3S or cement pastes, so it is not clear how the C-S-H gel formed in cement paste relates to this phase diagram.

Since the current data are for a multicomponent system, the calcium and silicon concentrations cannot be plotted directly onto the experimental phase diagram for the pure CaO-SiO₂-H₂O subsystem shown in Fig. 6. However, for any point on the phase diagram for the pure system, the IAP can be calculated by speciating the Ca and Si concentrations and calculating ionic activities using the procedure outlined in Section 4. The resulting values can then be compared to the corresponding IAP values for the cement pastes. Jennings [8] lists the approximate triple points where C-S-H and CH are in equilibrium as being 22 mM CaO and 1.5 µM SiO_2 for the lower curve and 22–27 mM CaO and 20 μ M SiO_2 for the upper curve. These points are indicated on Fig. 6 with larger circles. The IAP values for these points, along with the average value for later hydration times for the cement pastes, are listed in Table 6. As shown in Table 6, the IAP values for the cement pastes are close to the values for the intersection of the upper curve C-S-H and CH solubility lines. This suggests that the cement paste pore



Fig. 6. Collected solubility data in the pure CaO–SiO₂–H₂O system, after Jennings [8]. The data appear to define an upper (M) and a lower (S) C-S-H solubility curve. Estimated intersections of each C-S-H curve with the solubility of CH (invariant points) are shown as large circles.

Table 6 IAP values for C-S-H in cement paste and in the pure $\rm CaO-SiO_2-H_2O$ system

	log(IAP _{CB}) (Eq. (4))	log(IAP _{Gl}) (Eq. (5))	$log(IAP_K)$ (Eq. (6))
Lower curve	- 12.40	- 12.51	- 3.92
Upper curve (27 mM Ca)	- 11.03	- 11.14	- 3.72
Upper curve (25 mM Ca)	- 11.12	- 11.23	- 3.79
Upper curve (23 mM Ca)	- 11.22	- 11.33	- 3.88
OPC paste ^a	-11.28	-11.22	-3.77
WPC paste ^a	- 11.28	- 11.34	- 3.77

^a Average value for 3–28 days.

solutions are in equilibrium with C-S-H gel that is similar to the C-S-H formed during the hydration of dilute suspensions of C_3S powder.

6. Conclusions

For the first time, the elemental concentrations of Ca, Na, K, S, Al, and Si in the pore solutions of normal w/c cement pastes were monitored from shortly after mixing to nearly 28 days of hydration. Saturation levels in the two cements tested were very similar, despite the differences in pH and ionic strength that arose from their different alkali content. Calculations of the SI of portlandite and gypsum are in good agreement with previous work. SI calculations for the hydrated calcium sulfoaluminate phases indicate very high levels of supersaturation prior to the consumption of gypsum at around 12 h and more modest levels thereafter. At all times, ettringite was more supersaturated than calcium monosulfoaluminate.

The solubility behavior of C-S-H was investigated by applying three different IAP equations to the data. In each case, the IAP values for the two pastes were in good agreement after about 10 h. The IAP values declined gradually over time, indicating either a declining level of supersaturation with respect to C-S-H or a decrease in the solubility of the C-S-H gel with hydration time due to structural changes. The estimated invariant point in the pure CaO-SiO₂-H₂O system, representing equilibrium between portlandite and the upper C-S-H curve originally identified by Jennings [8], results in IAP_{C-S-H} values very similar to those calculated in the cement pastes at later times. This suggests a similarity between the C-S-H in normal w/c cement pastes and the C-S-H formed by stirring dilute suspensions of C₃S powder.

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