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Cement and Concrete Research 33 (2003) 2037–2047

CEMENT AND CONCRETE RESEARCH

Effect of hydration temperature on the solubility behavior of Ca-, S-, Al-, and Si-bearing solid phases in Portland cement pastes

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Received 18 December 2002; accepted 27 June 2003

Abstract

The concentrations of Ca, S, Al, Si, Na, and K in the pore solutions of ordinary Portland cement and white Portland cement pastes were measured during the first 28 d of curing at temperatures ranging from 5–50 °C. Saturation indices with respect to solid phases known to form in cement paste were calculated from a thermodynamic analysis of the elemental concentrations. Calculated saturation levels in the two types of paste were similar. The solubility behavior of Portlandite and gypsum at all curing temperatures was in agreement with previously reported behavior near room temperature. Saturation levels of both ettringite and monosulfate decreased with increasing curing temperature. The saturation level of ettringite was greater than that of monosulfate at lower curing temperatures, but at higher temperatures there was effectively no difference. The solubility behavior of C-S-H gel was investigated by applying an appropriate ion activity product (IAP) to the data. The IAP_{CSH} decreased gradually with hydration time, and at a given hydration time the IAP_{CSH} was lower at higher curing temperatures.

Keywords: Hydration; Temperature; C-S-H; Pore solution; DEF

1. Introduction

Temperature is a key variable affecting the curing of cement-based materials because it influences both the early hydration kinetics and the properties of the hardened cement paste or concrete. Although concrete initially gains strength more rapidly when cured at elevated temperatures, the final strength is lower and the permeability is higher. Elevated temperatures also reduce the tendency for irreversible creep and shrinkage. Most of these effects can be related to the increased rate of silicate polymerization at elevated temperatures [1–3], which densifies and stiffens the C-S-H as it forms. SEM studies [4–6] have shown that at elevated temperatures the outer-product C-S-H gel is denser and does not fill the capillary pore space as effectively, and thus the microstructure is more heterogeneous. Elevated temperatures may also alter the equilibrium assemblage of solid phases in cement paste. A particularly important example is the relative stability of ettringite and calcium monsulfoaluminate (monsulfate). During the early hydration period when sulfur concentrations in the pore fluid are high, ettringite is more stable than monosulfate at ambient temperatures. As the temperature increases, monosulfate eventually becomes the favored phase due to its smaller enthalpy of reaction. Lack of formation of ettringite during initial curing can lead to an expansive and damaging condition known as delayed ettringite formation (DEF) [7].

This study reports measurements of the concentration of major elements in pore solutions from two different types of cement paste cured at constant temperatures ranging from 5 to 50 °C over the first 28 days of curing. Of particular interest were any changes in the solubility behavior of C-S-H gel with temperature, and the changes in the calculated relative stability of ettringite and monosulfate as a function of temperature.

The hydration of cement produces solid phases in intimate contact with a pore system, and the composition of the pore solution can thus provide information about the hydra-

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doi:10.1016/S0008-8846(03)00224-2

tion products. Comparing the ion activity product for a solid phase with its equilibrium solubility product gives the degree of over or undersaturation, and tracking this saturation level over time, or comparing the levels in different types of paste, can be quite useful. Dilute suspensions of cement powder are not representative of normal cement paste and concrete, and thus hardened cement pastes should be used. Pore fluid can be extracted from cement paste after set by applying pressure to crushed paste with a steel die [8,9]. A number of studies of this type have been conducted (e.g., Refs. [10–15]), and the basic solubility behavior in the Na, K, Ca, S, and hydroxyl system has been established. Solutions become modestly supersaturated with respect to portlandite a few hours after mixing, and then saturation is approached slowly over a period of several days. Gypsum, which is present in the starting cement, is saturated during the first few hours of hydration and then undersaturated once it is consumed through reaction with C_3A to form less soluble calcium sulfoaluminate phases. The details of this process depend on the presence of free lime, the time to set, the presence of mineral admixtures, and other factors.

Few studies extending past the first few hours have reported concentrations of aluminum and silicon, which occur at such low concentrations that they are difficult to measure. Their neglect, while it does not significantly affect calculations for portlandite and calcium sulfate, prevents saturation levels of the calcium sulfoaluminate phases and C-S-H from being calculated. Exceptions include studies by Lawrence [13], Xue et al. [15], and recent work by the present authors [16], all conducted near room temperature. The latter study [16] reported elemental concentrations of Ca, S, Na, K, Al, and Si during hydration of two types of Portland cement at 20 °C, along with the saturation levels with respect to ettringite (AFt) and calcium monosulfate (AFm), as well as a few different ion activity products for C-S-H. The present study extends this work to different temperatures. In addition, data from the three studies noted above are reanalyzed to try to obtain a more complete picture of the solubility behavior of C-S-H gel in hydrating cement paste.

2. Experimental

Type I ordinary Portland cement (OPC) pastes were mixed at a water-to-cement ratio (w/c) of 0.4 by weight and hydrated under sealed isothermal conditions at 20, 30, 40 and 50 °C. White Portland cement (WPC) pastes were mixed at w/c = 0.5 and hydrated at 5, 20, 37, and 50 °C. The composition of the cements are listed in Table 1. The WPC has significantly lower alkali content than the OPC, and this, along with the higher w/c used to hydrate the WPC, led to significantly lower alkali contents and ionic strengths in the WPC pore solutions.

Table 1
Compositional data for ordinary and white Portland cements

	OPC (wt.%)	WPC (wt.%)
Element		
CaO	63.22	68.34
SiO_2	20.80	24.30
Al_2O_3	4.62	1.94
Fe_2O_3	2.57	0.37
MgO	4.15	0.59
Na_2O	0.16	0.13
K_2O	0.51	0.02
SO_3	2.70	2.01
Bogue mineralogy		
C_3S	58	72
C_2S	16	17
C_3A	7	5
C_4AF	12	1
Other		
Free Lime	0.41	1.57
LOI	0.90	1.58
Blaine surface area (m^2/kg)	312	446

Pastes were tested at times ranging from a few hours to 28 days. Prior to set, the pore fluid was collected by vacuum filtration using 0.22-μm filter paper in a glove box with flowing nitrogen. After set, hardened pastes were crushed and then compressed in a steel die to extract the pore fluid, using the procedure described by Barneyback and Diamond [8]. In both cases, care was taken to avoid carbonation.

Induction-coupled plasma atomic emission spectrometry (ICP-AES) was used to measure elemental concentrations of Na, K, Ca, S, Al, and Si within a few hours of pore fluid collection. ICP-AES can accurately measure micromolar elemental concentrations and is thus a particularly appropriate technique for measuring Al and Si in cement pore solutions.

3. Thermodynamic analysis

Calculating saturation levels requires measuring the elemental concentrations in the pore fluid and then performing a thermodynamic analysis to obtain ionic activities. In electrolytes such as cement pore solutions, each element exists as more than one ionic species. These species can be simple charged ions such as Ca^{+2}, or ion pairs such as $CaOH^{+}$ and $CaSO_4{}^{\circ}$. Calculating the equilibrium ionic activities from the elemental concentrations is an iterative process that is facilitated by the use of a computer program. In this study, the geochemical modeling program PHREEQC was used [17] with a thermodynamic database modified for cement paste. PHREEQC uses a single master aqueous species for each element, and the equilibrium activities of all ionic species in solution are calculated through a series of association constants, K_{ass}, which are simply equilibrium solubility products. The master species are H^{+}, H_2O, Ca^{+2}, H_4SiO_4, SO_4^{-2}, Na^{+}, K^{+}, and Al^{+3}. Table 2 lists the additional ionic species relevant to cement pore solutions, along with the ionic association equations and association constants.

The temperature dependence of the equilibrium solubility product, K_{sp}, for any reaction is related to the enthalpy of reaction, ΔH_r, by the van Hoff equation:

$$\ln(K_{sp}) = \ln(K_{sp(25C)}) + \frac{\Delta H_r}{R}\left(\frac{1}{298} - \frac{1}{T}\right) \tag{1}$$

where R is the gas constant and T is the temperature in Kelvin. Table 2 lists the values of ΔH_r used for each ion association constant.

For aqueous solutions with ionic strengths in the range of 0.1–0.5 M, activity coefficients can be calculated using an extended Debye–Huckel equation. The PHREEQC program is designed to use the WATEQ Debye–Huckel equation [18]:

$$\log_{\gamma_i} = \frac{-Az_i^2\sqrt{\mu}}{1 + Ba_i^0\sqrt{\mu}} + b_i\mu \tag{2}$$

where γ is the activity coefficient, z is the ionic charge, μ is the ionic strength, A and B are Debye–Huckel solvent parameters that depend only on temperature, a and b are ion-specific fitting parameters, and the subscript i refers to a particular ionic species. For some ions the fitting parameters are not known, in which case the Davies equation is used:

$$\log_{\gamma_i} = -Az_i^2\left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.3\mu\right) \tag{3}$$

The ion activity products of the solid phases of interest are listed in Table 3, along with their solubility product and enthalpy. It should be noted that PHREEQC considers numerous other solid phases but, as expected, none of these were found to be saturated (or nearly saturated) at any time or temperature. For portlandite and gypsum, the K_{sp} and ΔH_r are well known. For ettringite, a recent careful study [19] confirmed earlier measurements of the K_{sp} [20–23] and established the ΔH_r. Fewer solubility data for monosulfate have been published. Damidot and Glasser [24] measured a K_{sp} value for 25 °C, and in a separate paper published values for 50 and 85 °C [21], although experimental details are not given. These three values fell on a reasonably straight line on an Arrhenius-style plot, the slope of which supplied the ΔH_r value given in Table 3. For the C-S-H gel phase in cement paste, no commonly accepted equilibrium solubility product or enthalpy of reaction exists. The solubility behavior of C-S-H is thus investigated by monitoring the value of an appropriate ion activity product, as is discussed further in Section 4.4.

Table 2
Association constant and enthalpy of reaction for the ion association equations

Species	Formation	$\log(K_{ass})$ 25 °C	ΔH_r (kJ/mol)
OH^-	$H_2O - H^+$	– 14.00	55.81
$CaOH^+$	$Ca^{+2} + OH^-$	1.18	21.66
$CaSO_4°$	$Ca^{+2} + SO_4^{-2}$	2.11	5.44
$NaOH°$	$Na^+ + OH^-$	– 0.21	0.46
$KOH°$	$K^+ + OH^-$	– 0.46	– 20.71
$Al(OH)_4^-$	$Al^{+3} + 4OH^-$	33.3	– 46.26
$H_3SiO_4^-$	$H_4SiO_4° - H^+$	– 9.83	25.61
$H_2SiO_4^{-2}$	$H_4SiO_4° - 2H^+$	– 23.0	73.64

Data taken from the PHREEQC thermodynamic database [17].

Table 3
Thermodynamic data for the solid phases

Phase	Ion Activity Product	$\log(K_{sp})$ 25 °C	ΔH_r (kJ/mol)	Reference
Portlandite	$[Ca^{+2}]\,[OH^-]^2$	– 5.18	– 17.88	[17]
Gypsum	$[Ca^{+2}]\,[SO_4^{-2}]\,[H_2O]^2$	– 4.58	– 0.46	[17]
Ettringite	$[Ca^{+2}]^6\,[Al(OH)_4^-]^2\,[SO_4^{-2}]^3\,[OH^-]^4\,[H_2O]^{26}$	– 45.00	204.5	[19]
Monosulfate	$[Ca^{+2}]^4\,[Al(OH)_4^-]^2\,[SO_4^{-2}]\,[OH^-]^4\,[H_2O]^6$	– 29.43	45.57	[21,24] (see text)

4. Results and discussion

4.1. Elemental concentrations

Fig. 1 shows the total alkali (Na + K) concentrations in the OPC and WPC pastes at each temperature. The alkali concentrations in the OPC paste are significantly higher than in the WPC paste, as expected. In both pastes, alkali concentrations increase with time as the hydration reactions consume liquid water and concentrate the pore solutions. This process occurs more quickly at higher temperatures, leading to differences in the alkali concentration at earlier times. At later times the alkali concentrations tend to be lower in the pastes hydrated at higher temperatures. It is unlikely that the degree of hydration is lower at elevated temperatures after only 28 days of hydration. A contributing factor may be the lower bound water content of C-S-H gel hydrated at elevated temperature (e.g., Ref. [1]), which leaves more liquid water to dilute the alkalis at a given degree of hydration. A similar hypothesis has been proposed for differences in alkali concentrations arising from the addition of fly ash to cement [25].

The calculated pH values are shown in Fig. 2. For a given paste and temperature the pH value increases with time, in large part due to the increase in alkali concentration shown in Fig. 1. At a given temperature, the pH is higher in the OPC paste than in the WPC paste, again due to the differences in alkali content of the cements. In both pastes, the pH at all hydration times decreases with increasing temperature regardless of the relative alkali concentrations. This somewhat unexpected result arises from the increased rate of dissociation of water with temperature, which increases the hydrogen ion concentration. The hydroxyl ion concentration is dominated by the requirement to charge balance the alkali ions, and thus the pH is relatively unaffected by temperature despite the pH differences.

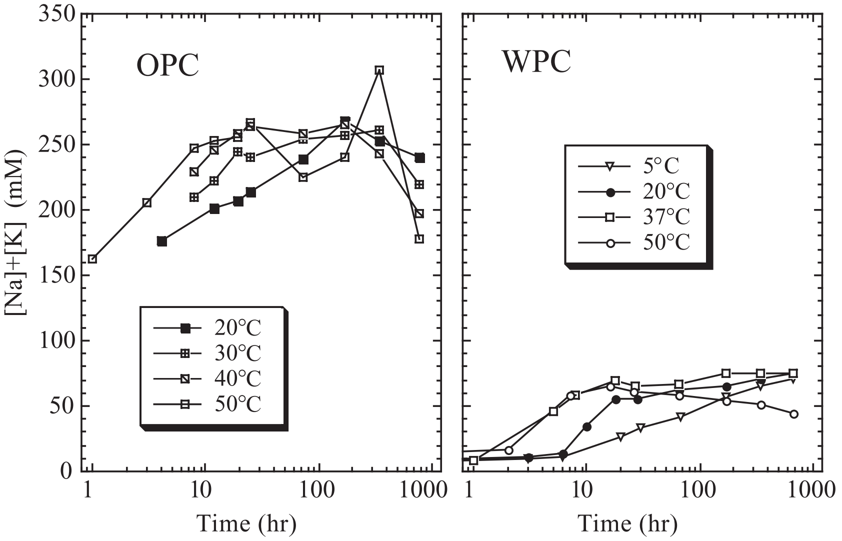

Fig. 1. Total alkali concentrations (Na + K) in the OPC pastes (left) and WPC pastes (right) as a function of hydration time.

The elemental concentrations of calcium and sulfur are plotted in Fig. 3. Calcium concentrations are significantly lower in the OPC paste. This is primarily due to the higher OH^- concentration in the OPC pore solutions, as both pastes are fairly close to saturation with respect to $Ca(OH)_2$ at all times. Calcium concentrations decline with time in both pastes, due to increases in pH as well as declining supersaturation levels with respect to $Ca(OH)_2$. Sulfur concentrations are initially much higher in the OPC paste. This is a result of the lower calcium concentration in the OPC pore solutions, as both pastes are close to saturation with respect to gypsum initially. Sulfur concentrations decline precipitously during the first several hours of hydration, due to the complete dissolution of the highly soluble gypsum. For both calcium and sulfur, the changes in concentration are accelerated by temperature, but the final values are relatively independent of temperature.

The elemental concentrations of aluminum and silicon are plotted in Fig. 4. Both are present at only micromolar concentrations. Aluminum concentrations show complex behavior that was difficult to interpret prior to the thermodynamic analysis. The final aluminum concentrations are not independent of curing temperature. In the OPC paste the aluminum concentration is much higher at lower temperatures, while in the WPC paste there is no clear trend. Silicon concentrations also show rather complex behavior that is difficult to interpret without considering equilibrium with respect to the C-S-H gel, which is done in Section 4.4.

4.2. Saturation levels of portlandite and gypsum

The calculated saturation levels of portlandite are shown in Fig. 5. In both pastes, the saturation level is highest after about 10 h of hydration and then declines gradually there-

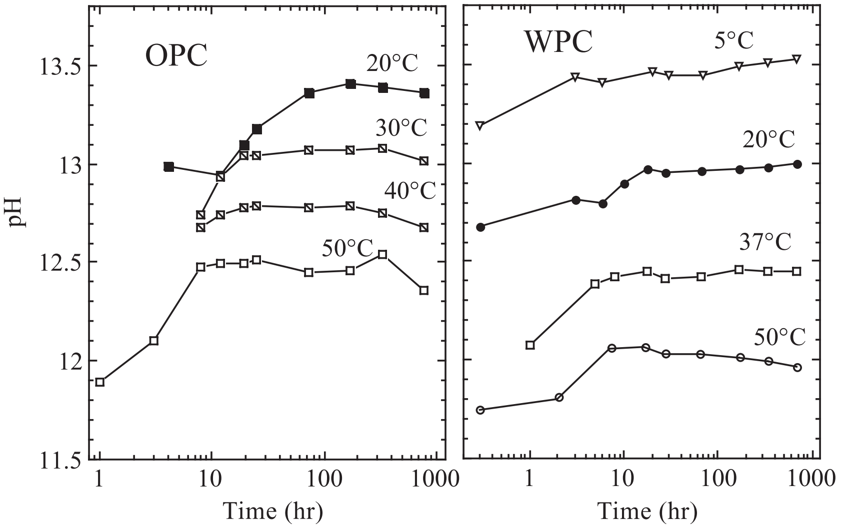

Fig. 2. Calculated pH in the OPC (left) and WPC (right) pore solutions as a function of time.

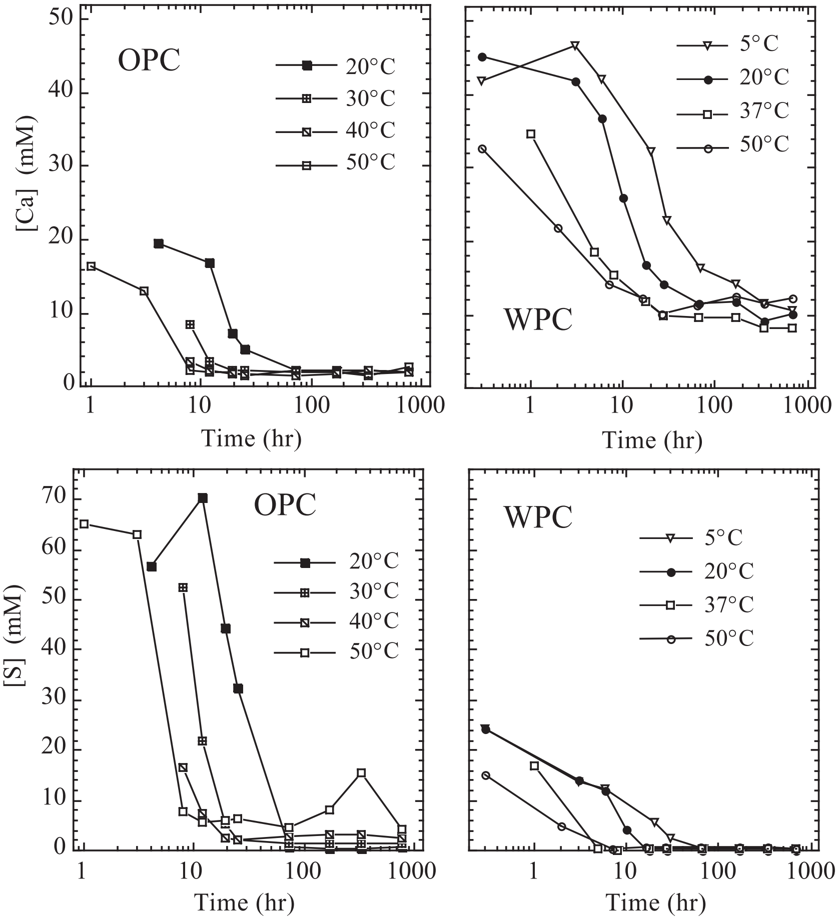

Fig. 3. Calcium (top) and sulfur (bottom) concentrations in the OPC (left) and WPC (right) pastes as a function of hydration time.

after, in agreement with previous findings. Saturation levels are higher in the WPC paste than they are in the OPC paste. At later hydration times, the saturation levels in each paste are slightly higher at higher temperatures. The reasons for the observed differences with paste type and temperature are not clear, but could be related to alkali content and crystal size, respectively.

The gypsum saturation levels are shown in Fig. 6. Both pastes are saturated in gypsum initially and then significantly undersaturated at later times after the gypsum initially present in the cement is consumed. As expected, the consumption of gypsum occurs more quickly when the curing temperature is higher. Modest supersaturation levels prior to 1 h of hydration may reflect the transformation of anhydrite into gypsum, as noted by Bailey and Hampson [10].

4.3. Saturation levels of the aluminate phases

Calculated saturation levels with respect to ettringite and monosulfate are shown in Fig. 7. Saturation levels with respect to both phases are very high initially, and then decrease after several hours. The timing of this decrease coincides with the consumption of gypsum. In both pastes, supersaturation levels decrease with increasing hydration temperature. The final saturation level with respect to ettringite is higher than that of monosulfate in both pastes at all temperatures (see Table 4), indicating that ettringite is the stable phase. However, the difference in supersaturation levels of ettringite and monosulfate decreases with increasing temperature, and for the OPC paste at 50 °C the difference in saturation levels is well within experimental error. This is consistent with calculations showing that monosulfate becomes the stable phase in cement systems at about 45–50 °C [21].

The calculated saturation levels shown in Fig. 7 raise a few questions. One is the much higher saturation levels calculated for the WPC paste as compared to the OPC paste. In the OPC paste, final saturation levels range from mild supersaturation to mild undersaturation, and all are with experimental error of saturation, particularly given the large stoichiometric coefficients used to calculate the ion activity products. However, given that the same experimental procedure and thermodynamic model was used for the WPC paste, the significantly higher saturation levels appear to be a real effect. High supersaturation levels often arise from a kinetic restraint for the formation of a phase. The declining levels of supersaturation with

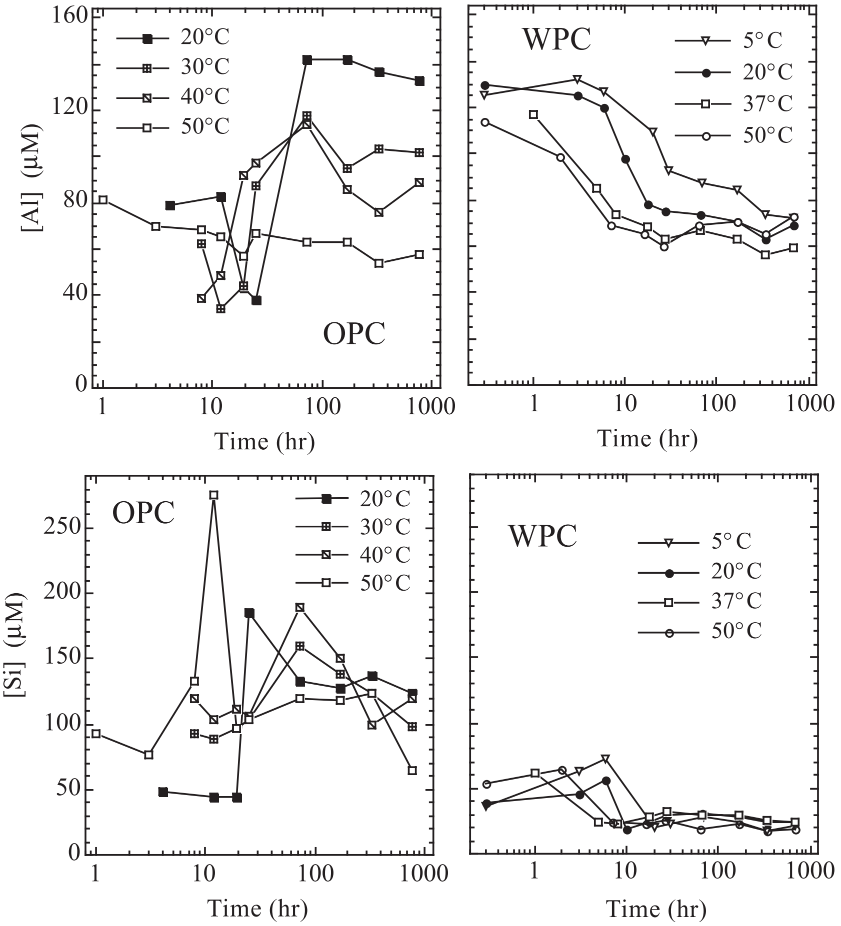

Fig. 4. Aluminum (top) and silicon (bottom) concentrations in the OPC (left) and WPC (right) pastes as a function of hydration time.

increasing temperature are consistent with a kinetic restraint on ettringite (or monosulfate) formation, as higher temperatures assist in overcoming kinetic barriers. However, the source of this kinetic restraint is not clear. The primary differences between the OPC and WPC are the higher alkali content and aluminate mineral content of the former. Alkalis have been shown to slightly retard the kinetics of ettringite formation [26,27], which would in-

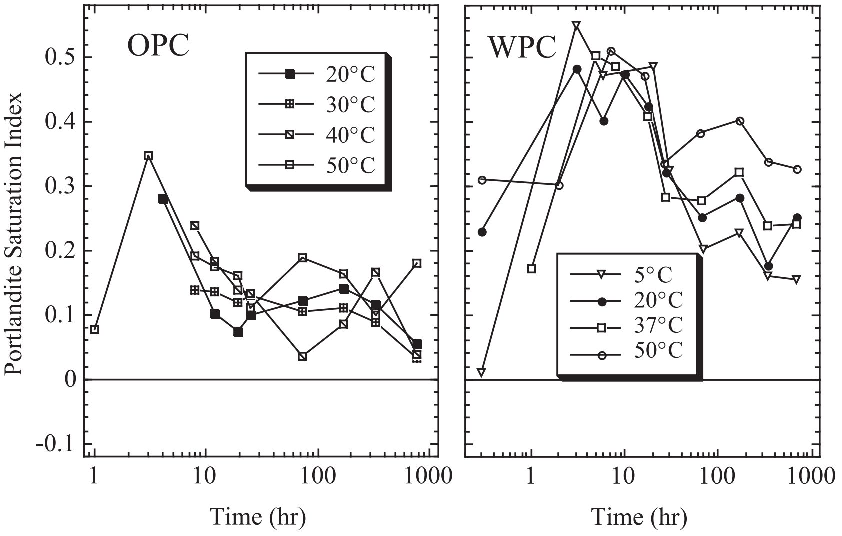

Fig. 5. Portlandite saturation index in the OPC (left) and WPC (right) pastes as a function of hydration time. A saturation index of zero indicates equilibrium between solid and liquid.

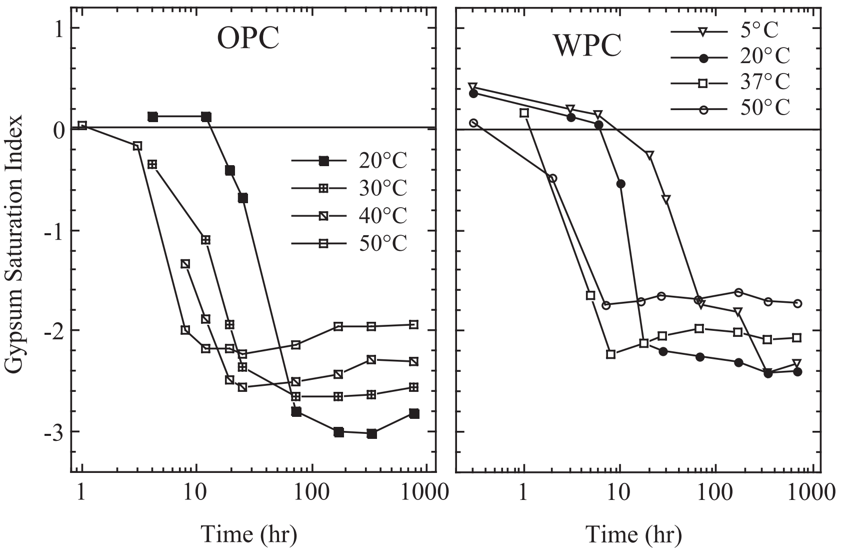

Fig. 6. Gypsum saturation index in the OPC (left) and WPC (right) pastes as a function of hydration time. A saturation index of zero indicates equilibrium between solid and liquid.

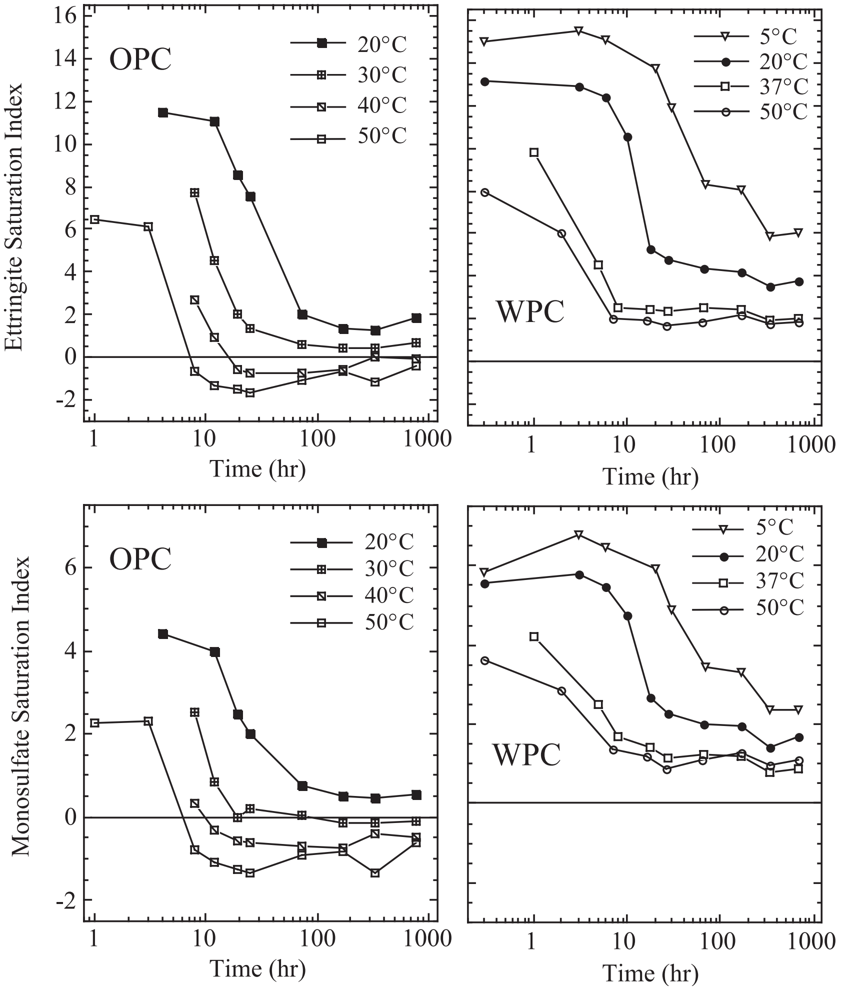

Fig. 7. Calculated saturation levels of the calcium sulfoaluminate phases ettringite (top) and monosulfate (bottom) in the OPC (left) and WPC (right) pastes. A saturation index of zero indicates equilibrium between solid and liquid.

Table 4
Final saturation indices of ettringite and monosulfate in the OPC and WPC pastes

OPC			WPC		
T (°C)	Ettringite	Monosulfate	T(°C)	Ettringite	Monosulfate
20	1.3	0.4	5	6.0	2.4
30	0.6	0.1	20	3.6	1.6
40	0.0	− 0.4	37	2.1	1.0
50	− 0.8	− 0.9	50	1.9	1.1

crease the supersaturation of the OPC paste relative to the WPC paste. If the degree of supersaturation at early hydration times is related to the rate at which the aluminates can dissolve into the solution, then the greater surface area of aluminate minerals in the OPC would lead to greater supersaturation in the OPC paste. Thus, it appears that neither of these factors can explain the present results.

Another issue is the different ionic strengths of the solutions, which can affect the relative accuracy of the activity calculations. The OPC pore solutions have an ionic strength of 0.35–0.4 M, while the WPC pore solutions have an ionic strength of about 0.1 M [16]. The WPC ionic strength is near the lower limit of applicability of the WATEQ extended Debye Huckel equation. The OPC value is within the reported upper limit of 0.5. However, such ion pairing models have been claimed to become inaccurate at ionic strengths as low as 0.2 [28]. Activity values were recalculated using the Davies equation for all ionic species. This lowered the IAP values in the WPC pastes somewhat; for example, the final SI value of ettringite in the WPC paste at 20 °C was lowered from 3.6 to 2.4. In the OPC pastes, use of the Davies equation increased the IAP values very slightly. These calculations do not change the conclusions, but give an idea of the errors involved in these types of calculations.

The present results indicate that ettringite is the stable phase at all times and temperatures studied, whereas the conversion of ettringite into monosulfate after the first day or so of reaction is an established phenomenon in cement hydration. Clark and Brown [27] hydrated C_3A and gypsum (at a 3:1 molar ratio) at different temperatures and NaOH concentrations, and found that the observed phase assemblages after the reaction was complete (ettringite and unreacted gypsum) were usually different from the equilibrium phase assemblages predicted by PHREEQC using the same starting solutions (monosulfate and portlandite in most cases). They attributed this discrepancy to the tendencies for slow reaction kinetics and metastable phase assemblages in this system. In another study, the same authors concluded that the AFm phase was increasingly stable as the alkalinity of the solution increased [29]. The present results are in agreement with this, as monosulfate saturation levels are closer to the ettringite saturation levels in the more-alkaline OPC paste then they are in the WPC paste.

4.4. Solubility behavior of C-S-H

Measuring and reporting the solubility of the C-S-H gel presents a challenge. C-S-H phases exist within a broad and continuous compositional range and the structure is variable even at a fixed composition. C-S-H also dissolves incongruently, so that the molar C/S ratio (C/S) of the solid will decrease or increase in response to changes in the solution. While pure C-S-H with C/S in the range of about 0.8–1.4 can be formed by precipitation from aqueous solutions or by direct reaction between CaO and colloidal silica, the C-S-H gel in cement paste, which has a higher C/S, forms only by the hydration of cement minerals under conditions of local supersaturation, and thus its solubility is difficult to measure directly and no K_{sp} value has been reported.

In general, phases that dissolve incongruently present difficulties for the solubility product approach, because the solubility product formula must correspond to the specific composition present at a given time. However, the composition and morphology of the C-S-H gel in cement paste is not thought to change significantly with hydration time (after the first few hours), and thus a C-S-H solubility product based on the average reported C/S of ∼ 1.7 is appropriate under normal conditions. In situations where portlandite is not present to buffer the calcium concentration, such as blended cements and pastes undergoing leaching or decalcification, this is of course not the case. The solubility behavior of C-S-H gel was investigated here by applying an ion activity product expression for C-S-H with C/S = 1.7 to the speciated pore solution data. The ion activity product expression first proposed by Glasser et al. [30] was used:

$$\begin{aligned}\mathrm{IAP_{CSH}} = {} & (\mathrm{Ca}^{2+})^{(3.5-y)/2}(\mathrm{CaOH}^{+})^{y/2}(\mathrm{H_2SiO_4^{2-}}) \\ & \times(\mathrm{OH}^{-})^{(3-y)/2}\end{aligned} \quad (4)$$

where y is the concentration of $CaOH^+$ ions in the solution divided by the sum of the Ca^{2+} and $CaOH^+$ concentrations. In Eq. (4), the C/S is 1.75 and the H/S is 1.75, a value close to measured values for solid C-S-H from cement paste with the liquid removed from the pores [7]. A recent, related study by the present authors [16] used Eq. (4) to monitor the solubility behavior of C-S-H in hydrating OPC and WPC pastes at 20 °C. Although calcium and silicon concentrations varied significantly over time and were very different in the WPC and OPC pastes, the ion activity product of C-S-H gel was quite stable for hydration times greater than about 10 h, and the IAP_{CSH} values in OPC and WPC pastes were very similar. Other IAP formulations applied to the same data gave similar results.

To properly evaluate the IAP_{CSH} expression, the concentrations of calcium, silicon, hydroxyl, and all other elements occurring in millimolar or greater concentrations in the pore solution must be known. In addition, the w/c must be low enough to be representative of normal cement and concrete. Lawrence [13] monitored OPC pore solutions at 25 °C

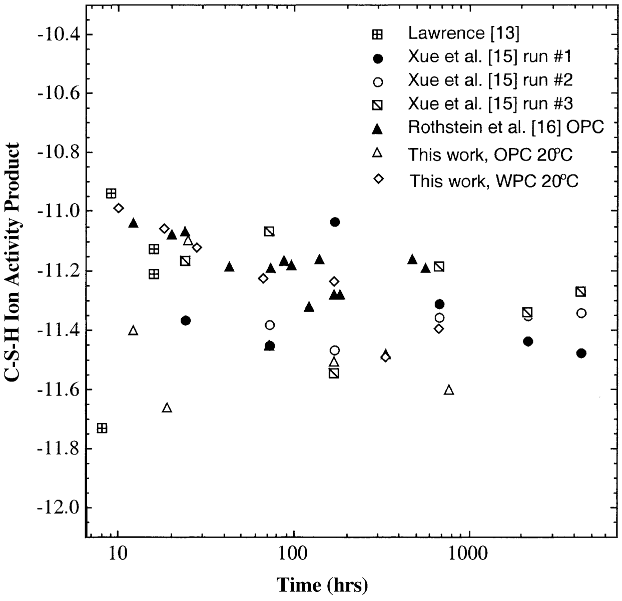

Fig. 8. C-S-H ion activity product in cement paste near 20 °C, calculated using Eq. (4). See text for more details.

during the early stages of hydration (up to about 20 h) at a variety of w/c, and his data from w/c = 0.5 meet the above criteria. Xue et al. [15] measured the concentrations of solutions expressed from hardened pastes with and without glass fibers at room temperature, for ages ranging from a few hours to 1 year. Concentration data from these two studies were speciated using the present approach and the IAP_{CSH} values were calculated using Eq. (4).

Fig. 8 shows the resulting IAP_{CSH} values from these two studies, along with the 20 °C values from the present and related earlier study. The values from the different studies are in quite reasonable agreement, as the variation from study to study is not very different from the scatter within an individual study. The IAP_{CSH} appears to decline gradually with time, and values for hydration times greater than 200 h fall within the range of -11.35 ± 0.2.

Fig. 9 shows the IAP_{CSH} values for OPC and WPC pastes hydrated at different temperatures. For each paste, higher temperatures tend to give lower IAP_{CSH} values, and this difference is greater at earlier hydration times. This behavior is more pronounced in the WPC paste, which has a greater temperature range and less scatter in the data for each paste. At times earlier than about 10 h, the WPC pastes have significantly higher IAP_{CSH} values than the OPC pastes, but, as noted earlier, the values for the two pastes converge at later times. A simple interpretation of the

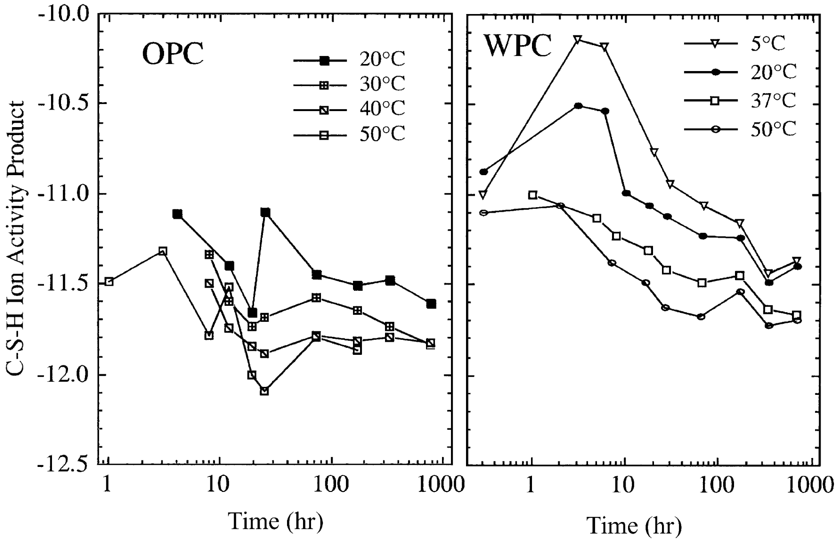

Fig. 9. C-S-H ion activity product at different hydration temperatures in the OPC pastes (left) and WPC pastes (right), calculated using to Eq. (4).

present results is that the IAP_{CSH} value decreases with the degree of hydration, so that higher hydration temperatures and longer hydration times lead to lower IAP_{CSH} values.

In general, a decrease in the observed ion activity product of a phase known to be present in the system could be caused by either a decrease in the equilibrium solubility product, a decrease in the level of supersaturation, or both. Supersaturation often occurs when reaction rates are high, and is less common in stable systems. It thus appears likely that the values of IAP_{CSH} toward the end of the experiment give a good measure of the equilibrium solubility product for the C-S-H gel present in those pastes. At earlier times, when the IAP_{CSH} values are declining more rapidly, the situation is less clear; the declining IAP_{CSH} could be due to decreasing supersaturation with respect to a fixed K_{sp} value, as is observed for portlandite, or changes in the K_{sp} value itself.

Gradual structural changes in the C-S-H gel are known to occur with time, most notably an increase in the degree of polymerization of the silicates. In addition, the degree of polymerization for a given hydration time or degree of hydration increases with temperature [2]. Making the reasonable hypothesis that increased polymerization would lead to lower solubility, this can explain the observed trends in the solubility behavior of C-S-H.

5. Summary

The elemental concentrations of Ca, S, Al, Si, Na, and K in the pore solutions of normal w/c OPC and WPC pastes hydrated at temperatures in the range of 5–50 °C were reported for the first time. Changes in the saturation levels during the early period of hydration occurred more rapidly at higher curing temperatures, as expected. At all temperatures, portlandite exhibited small and decreasing levels of supersaturation, and gypsum was saturated during the first few hours and greatly undersaturated thereafter, in agreement with previously established behavior near room temperature.

In general, the hydrated calcium sulfoaluminate phases exhibited modest levels of supersaturation after the first several hours of hydration. The levels of supersaturation were higher in the WPC paste than in the OPC paste at all times and temperatures, and for both pastes the levels decreased with increasing hydration temperature. The aqueous phase in both pastes was more saturated with respect to ettringite than monosulfate near room temperature, but at 50 °C the levels of saturation of ettringite and monosulfate were equal within experimental error in each paste.

The solubility behavior of C-S-H gel was investigated by applying an appropriate ion activity product to the data. Reanalyzed data from a few different studies performed near room temperature, including the present study, were in agreement: the IAP_{CSH} decreases gradually as hydration progresses and reaches a value of -11.35 ± 0.2 for the selected ion activity product. The IAP_{CSH} in both pastes from the present study decreased with increasing curing temperature, and this difference was greater at early hydration times. The effect of temperature on the solubility behavior may be related to the degree of polymerization of the silicates in the C-S-H gel.

Acknowledgements

This work was supported by the National Science Foundation under contract CMS-007-0922.

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