Solubility of Zn(II) in Association with Calcium Silicate Hydrates in Alkaline Solutions

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The binding of Zn(II) to the cement mineral calcium silicate hydrate (CSH) was investigated in a well-defined laboratory system. CSH (Ca:Si = 1:1) was synthesized by coprecipitation with varying contents of Zn(II). Zn(II) was added in the proportions 0, 0.1, 1.0, 5.0, and 10% in exchange for Ca. The resulting CSH was characterized by X-ray diffraction. The solid phases were then equilibrated in aqueous suspensions, and the solubilities of Ca, Si, and of Zn(II) were determined as a function of pH and Zn(II) content in the solid phase. The solubility of Ca and Si in equilibrium with the CSH phases was in agreement with that predicted by thermodynamic calculations. Dissolved Zn(II) concentrations were below the solubility of ZnO and directly related to the concentration in the solid phase. It was postulated that solid solution is the mechanism by which Zn(II) is bound in the CSH matrix.

Introduction

Cement is in common use worldwide for the stabilization of hazardous and radioactive waste (*1*). The main objective is to reduce the mobility of contaminants first by reducing the permeability of the wastes and thereby minimizing the possibility of interactions with percolating waters and second by geochemically binding the contaminants in the cement matrix. In two excellent reviews by Cougar et al. (*2*) and Cocke and Mollah (*3*), the mechanisms of waste stabilization in the cement matrix are described. Studies appear to have determined three possible mechanisms. A metal ion may either be bound in the alkaline cement matrix as an oxide or mixed oxide, be sorbed to surfaces, or be incorporated into cement minerals. According to these authors, ettringite ($3CaOAl_2O_3CaSO_4 \cdot 32H_2O$) and calcium silicate hydrate ($CaOSiO_2 \cdot xH_2O$ or CSH) are prime candidates for heavy metal binding because of their abundance and appropriate structures.

The formation of calcium zincate ($CaZn_2(OH)_6 \cdot 2H_2O$) has been suggested to control Zn solubility in cementitious systems and has been observed by a number researchers (e.g., ref *4*), but there is evidence to show that this is an intermediate product that is no longer detectable after a few days (*5*). Mollah and co-workers (*6*) have suggested that surface sorption could control Zn solubility, but they have yet to prove this mechanism. Recent work has indicated that heavy metal cations may substitute for Ca(II) and be incorporated in CSH (*7*). The structure of CSH is microcrystalline or almost amorphous with alternating layers of silica tetrahedra and CaO (*8*).

In this paper, the results of preliminary experiments carried out to determine the binding mechanisms of Zn(II) in a CSH matrix are reported. The focus of this work is the interpretation of the aqueous chemistry of CSH/Zn(II) mixtures in terms of binding mechanisms.

Methods

All solutions and preparative steps were carried out under Ar. CSH with a C:S ratio of 1:1 was prepared according to the method of Suzuki et al. (*9*). The CSH produced is CSH(I), akin to tobermorite (*8*). A CSH suspension was prepared in a polyethylene bottle in which $Ca(NO_3)_2$ (26.4 g) was dissolved in ethanol (75 mL). Tetraethyl orthosilicate (25 mL, Merck 800658) was added to this solution followed by 850 mL of 1.2 M NaOH solution while stirring vigorously. The mixture was stirred for 24 h, centrifuged, rinsed with up to 10 L of a 3 mM $Ca(OH)_2$ solution until the pH of the leachate was below 12, and freeze-dried. It was necessary to add Ca to the rinsing water in order to avoid selective leaching of Ca(II). $Zn(NO_3)_2$ was substituted for $Ca(NO_3)_2$ in the molar proportions 0.1, 1, 5, and 10%. X-ray analysis (Scintag XDS 2000, Co-Kα source, Diffraction Management Systems software, single analyses after around 8 h, and 1, 3, 7, 28, and 100 days) determined no calcite or portlandite ($Ca(OH)_2$) in the solid phases but identified peaks characteristic of CSH gels (JCPDS 33-0306). Furthermore, the presence of insoluble SiO_2 and calcite residues (*8*) was determined from portions of the prepared solids (1 g) dissolved in methanolic salicylic acid solutions (7% per weight). The yield of the CSH preparation was found to be over 99%. Zinc (hydr)oxides or calcium zincate were not detected in samples aged 1 week or more.

Solubility experiments were carried out on the CSH samples and on commercially available ZnO (Merck) in triplicate. The sample (0.3 g) was placed in a polyethylene tube (50 mL) together with 30 mL of deionized water and made up to 2 mM NaOH and from 0 to 7 mM HNO_3 (using 1 M stock solutions of acid and base). The suspensions were equilibrated at 25 °C under Ar for 24 h. (In a preliminary experiment using CSH−Zn 10%, at pH 11.7 and 9.4, suspensions had been equilibrated for a total of 15 days, and it had been determined that only 24 h was required for equilibration.) Subsequently the pH of a portion of the suspension was measured and the rest was filtered (0.45 μm). Solutions with a pH value above 7 were acidified to pH 2 with HNO_3 (1 M).

Measurements of pH were made using a pH meter (Metrohm 691) and Dosimat titrator (Metrohm 665). The electrode (Ross combination, Orion model 81-72BN) was calibrated using a titration technique. Standard potentials and slopes were determined by nonlinear regression from the calibration data, and the log $[H^+]$ values of aqueous solutions were determined from the calibration constants. Ca(II) and Si(IV) were determined by inductively coupled plasma optical emission spectrometry (ICP−OES, Spectroflame M). Zn(II) was determined using differential pulse anodic stripping voltammetry (693 VA Metrohm processor and 694 VA Metrohm Stand). To a 10-mL aliquot of sample, KNO_3 (1 M, 0.1 mL) and a buffer solution (0.6 mL, pH 4.74, 1:1 mixture of 2 M CH_3COOH and NH_3) were added.

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10.1021/es9808651 CCC: $18.00
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Published on Web 05/15/1999

TABLE 1. Total Zn Concentrations in Equilibrium with CSH−Zn[a]

sample	H^+ (mmol g^{-1})	pH	Zn (μM)	sample	H^+ (mmol g^{-1})	pH	Zn (μM)
CSH 0.1%	−0.2	12.42	0.044	CSH 5%	−0.2	12.21	3.0
	0.0	12.04	0.015		0.0	10.96	0.17
	0.2	11.23	0.003		0.2	9.69	0.03
	0.4	10.11	<0.006		0.4	9.08	0.02
	0.7	9.26	<0.006	CSH 10%	0.0	12.24	9.9
CSH 1%	−0.2	12.33	0.37		0.2	11.78	4.4
	0.0	11.7	0.06		0.4	10.82	0.62
	0.2	10.54	0.008		0.7	8.99	0.16
	0.4	9.46	0.005				
	0.7	9.01	0.004				

[a] The data shown are the average triplicate measurements. The detection limits are close to 6 nM. A negative sign in the column showing the quantities of acid added denotes the addition of base. Note that the pH values depend on the degree of sample washing during sample preparation.

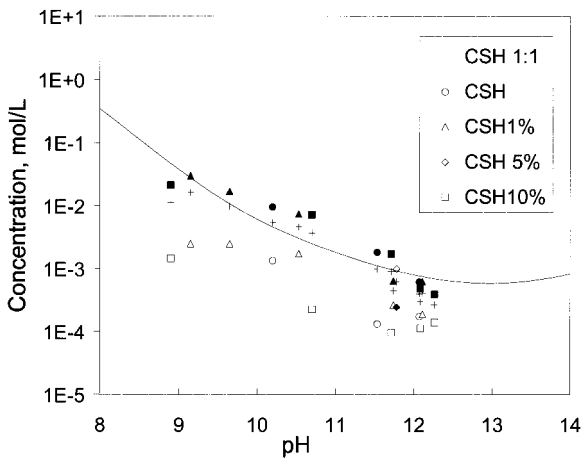

FIGURE 1. Total dissolved Ca (filled symbols) and Si (open symbols) concentrations as a function of pH. The crosses represent $\sqrt{[Ca]\cdot[Si]}$. The line represents estimated solubilities of Ca and Si in equilibrium with CSH with Ca:Si = 1:1 for $I = 0.01$ and $K_{so} = 14.98$ (*12*).

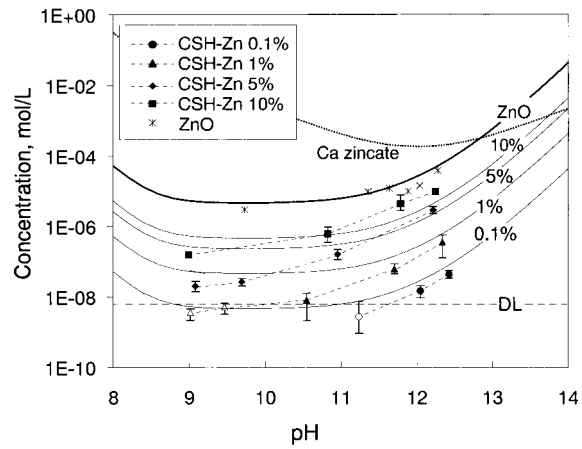

FIGURE 2. Measured and estimated Zn(II) concentrations as a function of pH. The solid lines represent model calculations. The dashed lines serve as eye guides for the data of a particular CSH composition. The error bars represent confidence (95%) of the triplicate measurements. The open symbols represent data points that are significant but below the detection limit determined as described in the text.

Preconcentration was carried out at −1150 mV for 90 s. With a sweep rate of 10 mV/s and a step of 50 mV, a voltamogram was recorded between −1150 and −800 mV. The detection limit determined from the standard deviation of 10 blanks was found to be 6 nM.

Thermodynamic calculations were made with the program MQV40TIT (*10*) using compiled thermodynamic data (*11*). Measured Ca(II) and Si(IV) concentrations were compared to values predicted to be in equilibrium with CSH (Ca:Si = 1:1, log K_{so} = 14.98 *12*) alone (see Table 1). It was found that in conditions less alkaline the measured Zn concentrations were compared with a simplified solid solution approach described later in the text and with the reported solubility of Zn in equilibrium with calcium zincate (K_{so} = 45.8; *4, 13*). Activity corrections were made using the Davies equation for an average ionic strength of 0.01. The maximum ionic strength encountered at pH 9 was 0.063.

Results and Discussion

The total dissolved concentrations of Ca and Si are shown as a function of pH in Figure 1. The solubility of Ca and Si is close to that predicted by thermodynamic calculations in the presence of CSH alone. Zinc appears to have no measurable effect on the solubility of the CSH. Below pH 9 significant quantities of CSH are dissolved (>10%). The concentrations of Ca and Si above pH 12, determined in the presence of NaOH, are slightly lower than predicted. It should be noted that in all but one experiment Ca concentrations are higher than Si concentrations because of incongruent dissolution. Ca appears to be preferentially leached from the CSH. This is a common observation that has led researchers to believe that CSH is in fact a solid solution of $Ca(OH)_2$ and CaH_2SiO_4 (*12, 14, 15*).

The solubility of Zn(II) has been plotted as a function of pH in Figure 2. The crosses denote the solubility of Zn(II) in the presence of ZnO alone. The solid lines represent model calculations. The agreement between the model calculations and the data for ZnO is good. For the CSH−Zn mixtures, the Zn(II) concentrations in solution correlate directly to the Zn(II) content of the solid phase for a given pH value. The concentrations of Zn(II) in equilibrium with the CSH−Zn 1.0% solid are approximately 1 order of magnitude greater than those in equilibrium with CSH−Zn 0.1% and a little more than 1 order of magnitude lower than the CSH−Zn 10% concentrations. The solubility curves run parallel to the solubility curves of ZnO.

The solubility control of Zn(II) in the CSH−Zn solids does not appear to be controlled by the formation of Zn(II) containing solids of a single composition. This can be deduced from the positive correlation between aqueous and solid-phase concentrations of Zn. In other words, Zn solubility does not appear to be controlled by either calcium zincate or ZnO, since measured concentrations are significantly lower than predicted (Figure 2).

The two possible mechanisms that could explain the observed behavior between concentrations in the solid phase and in solution are sorption and solid solution. With these

preliminary experiments, neither mechanism can be excluded. The surface area of CSH is very large (undried up to 400 $m^2 g^{-1}$ and dried between 100 and 200 $m^2 g^{-1}$; *8*) and has a large potential for metal uptake. However, it is difficult to characterize the surface of such a soluble and microcrystalline solid as CSH.

In our preliminary interpretation, we assume solid solution to be the predominant binding mechanism. In a first approximation, we assume the end members to be CaO and ZnO. This choice is made because zinc(II) silicates do not appear to be formed at room temperature and because the incorporation in the interstitial CaO layers of the CSH is the most likely alternative. The solubility of Zn(II) can thus be described by the following equation (e.g., *16*):

$$a_{Zn} = K_{ZnO}\lambda_{ZnO}X_{ZnO}[a_{H^+}]^2 \quad (1)$$

where K, λ, X, and a represent the solubility product, the solid activity coefficient, the mole fraction, and the solution activity, respectively. From eq 1, the expected solubility of Zn(II) can be estimated as a function of X and pH. In the absence of further information, ideal mixing is assumed (i.e., $\lambda_{ZnO} = 1$). In Figure 2, the expected Zn(II) concentrations are shown as a function of pH. Experimental data and estimates agree quite well, particularly above pH 11. Below this pH value, the estimated concentrations are approximately 1 order of magnitude above the measured values. The reasons for this are unclear.

Solid solution is a possible binding mechanism for Zn(II) in CSH. The initial results indicate that at least 10% of Zn may be incorporated in the CSH structure. Although solid solution may be the predominant mechanism, the possibility of surface binding is yet to be investigated. This challenging work may lead to new modeling approaches in the assessment of inorganic waste materials in cementitous media.

Acknowledgments

We acknowledge Sandro Brandenberger for tackling this difficult task in the laboratory. We further thank Arnold Stahel, Geology Department, ETHZ, Zürich, for his assistance with XRD measurements.

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Received for review August 24, 1998. Revised manuscript received March 17, 1999. Accepted April 5, 1999.

ES9808651