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The solubility of calcium zincate ($CaZn_2(OH)_6{\cdot}2H_2O$)

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Abstract

Ca zincate ($CaZn_2(OH)_6{\cdot}2H_2O$) plays an important role in the geochemical behaviour of Zn in cementitious systems. This paper describes the determination of a solubility product for Ca zincate and its range of application. Calcium zincate was synthesized and characterised by X-ray diffraction (XRD). Samples were then equilibrated at 25°C and an ionic strength of 0.1 M in a pH range between 11.4 and 12.7. A solubility product, $\log K_{s0} = 43.9$, was determined for infinite dilution using the Davies equation for the following reaction.

$$CaZn_2(OH)_6{\cdot}2H_2O_{(s)} + 6H^+_{(aq)} \leftrightarrow Ca^{2+}_{(aq)} + 2Zn^{2+}_{(aq)} + 8H_2O$$

The solubility product can be used to successfully interpret the results of experiments in which Zn is equilibrated with C-S-H(I) at pH values between 11.7 and 12.78 at 25°C and an ionic strength of 0.1 M. However, the solubility product is not able to model both the Zn and Ca concentration at a given pH value because dissolution is incongruent. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Calcium-silicate-hydrate (C-S-H); Thermodynamic calculations; Zinc; Heavy metals

1. Introduction

Interest in the mobility and fate of heavy metals in cements has increased over the past years because of the use of wastes as secondary materials in cement production and because of the use of cement to immobilise heavy-metal- and radionuclide-containing wastes [1,2]. Because most of heavy metal cations are relatively insoluble or amphoteric in alkaline solutions, cement generally reduces their mobility over longer periods. In addition to this pH effect, there are often very specific and strong interactions between cement components and waste ions, which further depress aqueous concentrations [3]. These interactions are generally attributed to sorption processes, but the exact mechanisms are not yet well understood calcium-silicate-hydrate (C-S-H) gel, with its high specific surface area and range of sorption sites, is usually the main source of the sorption potential. The more crystalline hydrates are believed to favor crystallochemical substitution reactions [3,4], the most prominent example probably being ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$).

There was a quite early interest in the chemical reactions of Zn with cement minerals, because Zn is known to interact with the cement clinker grains during hydration and to retard setting. Lieber and Gebauer [5] demonstrated with X-ray diffraction (XRD) the intermediate formation of the crystalline calcium zincate ($CaZn_2(OH)_6{\cdot}2H_2O$) during the retardation period. After some days of reaction, the calcium zincate was no longer detectable, but a new solid Zn phase could not be detected. With the aid of microprobe analysis, they concluded that Zn was incorporated into C-S-H gel. Later Poon et al. [6] investigated the Zn release from a cementitious matrix by leaching tests, scanning electron microscopy (SEM) and XRD measurements. They concluded that $Ca(OH)_2$ was the major phase involved in the fixation reaction and that C-S-H was unlikely to be involved in the fixation mechanism. X-ray absorption fine structure spectroscopy (XAFS) measurements by the same authors [7] identified Zn in a cementitious matrix as coordinated by a first shell of four oxygens and a second shell consisting of a mixture of OH and Si atoms. They interpreted the results as further evidence for the model of

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calcium zincate surface precipitation. Combined X-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS), SEM coupled with energy dispersive spectroscopy (EDS), and Fourier transformed infrared spectroscopy (FTIR) analysis by Cocke and Mollah [8] confirmed the presence of calcium zincate, and they proposed the preferential deposition of Zn on the surface of the cement grains. In light of these results, Mollah et al. [9] proposed a charge dispersal model for the adsorption of Zn on the negatively charged cement particles and the subsequent formation of surface coatings of calcium zincate. Cocke et al. [10] derived a solubility constant for calcium zincate from literature data. With the aid of equilibrium model calculations, they suggested that the growth of calcium zincate on the cement particle surfaces was preceded by surface complex formation.

Further evidence appeared to suggest a more intimate interaction with C-S-H. Recently, Moulin et al. [11] suggested, on the basis of sorption isotherm and ^{29}Si NMR measurements, that structural retention by SiOZn bonds is involved in the sorption of Zn to C-S-H gel. Further XAFS analysis revealed that Zn is probably linked to SiO_4 tetrahedra at the end of the silica chains in C-S-H [11]. Johnson and Kersten [12] measured the solubility of coprecipitates of C-S-H(I) and Zn. The dissolved Zn concentrations could be directly related to the Zn concentration in the solid phase and, therefore, they postulated a solid-solution mechanism for the Zn sorption to C-S-H(I). In an investigation of Zn sorption to C-S-H(I), Ziegler et al. [13,14] observed that Zn diffuses into the C-S-H(I) particles, but does not appear to exchange for Ca and is therefore most probably not solid-solution formation in a classic sense but taken up into the interlayer of C-S-H(I). Their XAFS measurements were in agreement with the aforementioned studies and suggested that Ca was not in the second atomic shell surrounding Zn, but that ZnOSi bonds may be involved. They did, however, find that Ca zincate was formed at high Zn concentrations at a pH of above 12.

Calcium zincate obviously plays an important role in the chemistry of Zn in cement pastes and it is of importance to be able to understand the regions of stability and the solubility of Zn at equilibrium with this mineral. Since there is little available data, it was thought necessary to determine the solubility product of Ca zincate under controlled conditions. This paper presents results of solubility measurements of Ca zincate determined under controlled conditions at 25°C and an ionic strength of 0.1 M.

2. Experimental methods

2.1. Materials

All chemicals were at least of p.a.-grade. Solutions were generally prepared using 17 MW ultrapure water (Barnstead Nanopur), which was filtered through a 0.2-μm in-line filter. Before use, the ultrapure water was boiled and cooled to 20°C under argon.

In order to prevent a CO_2 contamination of the samples during preparation, all procedures involving alkaline solutions and solids were performed in a glovebox in an argon atmosphere with $p\text{CO}_2 < 1$ ppm. The solids were stored in desiccators above soda lime and NaOH pellets.

The glassware and HDPE flasks used for the experiments and analyses were leached with acid (~ 0.6 M diluted from concentrated HNO_3) for at least 24 h. Filtration was performed in a polycarbonate filtration unit (Sartorius) using membrane filter discs (0.45-μm nylon, Whatmann) in a nitrogen atmosphere or under vacuum.

Calcium zincate was prepared according to the method of Sharma [15]. In a 1000-ml HDPE bottle, 5 g of ZnO were dissolved in 500 ml of a 20% (w/w) KOH solution. Then successively, 50 g $Ca(OH)_2$, 73 ml water, and 109.85 g ZnO were slowly added to the KOH solution, which was continuously stirred. The bottle was sealed tightly and shaken for the next 48 h on a rotary shaker (Bühler, Swip SM 25) at 200 rpm. After that, calcium zincate was allowed to settle, and the liquid above it was decanted. The solid phase was washed with water on a vacuum filtration unit until the solution attained a pH value of about 7. The solid was freeze-dried (Leybold Lyovac GT 2) and subsequently examined by X-ray powder diffraction (XRPD, Scintag XDS 2000) used along with a copper X-ray tube (Cu-Ka, 1.5406 nm, 2000 W, 45 kV, 40 mA). The scans were collected in a range of 2θ from 2° to 70° at a rate of 0.03°/min. The original diffractograms were processed for background subtraction and peak identification using the software DMSNT from Scintag. The Powder Data File (PDF) database was supplied by the International Center for Diffraction Data (ICDD). The typical *d*-spacings obtained from samples in this work are in agreement with published data (Table 1, [15,16]) and the ICDD reference spectra (PDF no. 24-222 and 25-1449).

Four batches were produced in the same way and the resulting solid was intermixed. A particle size fractionation was performed by using metal-free analytical sieves with mesh sizes of 200, 100, and 63 μm. Most particles had a size between 100 and 200 μm; this fraction was used for solubility experiments.

2.2. Solubility determination

The solubility of calcium zincate was examined in batch experiments. In order to examine the influence of equilibration time and particle size on the solubility, preliminary experiments were conducted with calcium zincate of the size fractions > 100 and < 100 μm, previously equilibrated for up to 4 months in a 0.1-M NaCl electrolyte solution. It appeared that equilibrium was attained within 28 days and that the particle size had no influence on the solubility (Fig. 1).

Table 1
XRD data for Ca zincate

Present work			Sharma [15]		Liebau and Amel-Zadeh [16]	
2θ (°)	*d* (nm)	Relative intensity	*d* (nm)	Relative intensity	*d* (nm)	Relative intensity
14.15	6.258	76	6.237	8	6.254	45
17.54	5.015	12	5.008	9	5.052	14
21.56	4.134	6	4.116	8	4.118	19
22.58			3.926	8	3.935	20
28.55	3.121	100	3.123	9	3.124	100
30.98	2.89	9	2.881	10	2.884	43
31.7	2.815	5	2.814	7	2.820	33
32.96	2.708	5	2.706	5	2.715	16
36.23					2.477	16
36.56	2.456	10	2.454	6	2.456	18
37.61			2.38	5	2.390	36
38.54			2.322	1	2.334	13
46.28			1.964	5	1.960	17
46.64	1.946	7	1.946	4	1.946	26
48.35			1.882	3	1.881	13
50.06	1.821	8	1.82	7	1.821	10
52.61			1.739	3	1.738	15
58.52	1.576	7	1.577	6	1.576	22
62.3					1.489	11

The solubility experiments were performed with the 100–200-μm size fraction and an equilibration time of 28 days. Calcium zincate (5 g) was weighed in a 50-ml HDPE centrifuge tube. An aliquot of a 0.1-M NaCl electrolyte solution (35 ml) containing different amounts of acid or base was added. A high solid-to-liquid ratio was chosen in order to avoid changes in the composition of the solid phase. The solutions were prepared using 1.0 M stock solutions of NaOH and HCl, and the ionic strength was adjusted to 0.1 M by adding appropriate amounts of a 2.0-M NaCl stock solution. After filling, the tubes were sealed tightly with screw cap and Teflon tape. All samples were prepared in duplicate and equilibrated with wrist action shaking (Heidolph REAX 2) at a constant temperature of 25°C.

After equilibration, the suspensions were centrifuged at 8000 rpm for 30 min. The pH of the solution was measured in a 10-ml aliquot of the supernatant. The remaining solution was carefully decanted and filtered. The acidified solution (0.2 ml of concentrated HNO_3) was analyzed for Ca and Zn content. All experiments were carried out in duplicate. Since possible mineral impurities and changes in the solid phase could influence the solubility, the experiments were repeated twice sequentially with the same aliquot of solid samples.

The pH was measured as proton concentration using a combination glass electrode (Metrohm 6.0202.100) connected to a digital voltmeter (Metrohm 713). The electrode was calibrated by titrating 25 ml of a 0.01-M HCl solution with up to 15 ml 0.05 M NaOH using a dosimat (Metrohm 665). Both solutions were prepared by diluting commercially available 1.0-M standard solutions in the glovebox with a constant ionic strength of 0.1 M NaCl as electrolyte. Standard potentials and slopes were determined by linear regression over the acidic and alkaline parts of the pH scale. The calibrations and all measurements were carried out under argon.

The dissolved Zn concentrations were measured by atomic absorption spectrometry (AAS, Perkin-Elmer 5000) at 213.9 nm in an acetylene–air flame. The calibration was carried out with five standard solutions between 0.050 and 1.0 ppm. All measurements were performed in triplicate and were checked for matrix effects by analyzing some samples by standard addition.

The dissolved Ca concentrations were measured by AAS (Perkin-Elmer 5000) at 422.7 nm in an acetylene–nitrous oxide flame. The measurements were carried out in 0.05-M KCl solutions as ionization buffer. The calibration was carried out with five standard solutions between 0.1 and 2.0 ppm. All measurements were performed in triplicate and were checked for matrix effects by analyzing some samples with standard addition.

The accuracies of the measured Zn, Ca, and OH^- concentrations were estimated from the data of the duplicate samples together with the repeated analyses. The resulting confidence intervals for the measured concentrations at a probability of 95% are generally $\Delta[Zn] \leq \pm 5\%$, $\Delta[Ca] \leq \pm 5\%$, and $\Delta[OH^-] \leq \pm 5\%$.

Thermodynamic equilibrium calculations were performed with the aid of the computer programs MQV40TIT [17], based on MICROQL by Westall [18] and FITEQL [19]. Thermodynamic data are listed in Table 2. The values were corrected for an ionic strength of 0.1 M in accordance

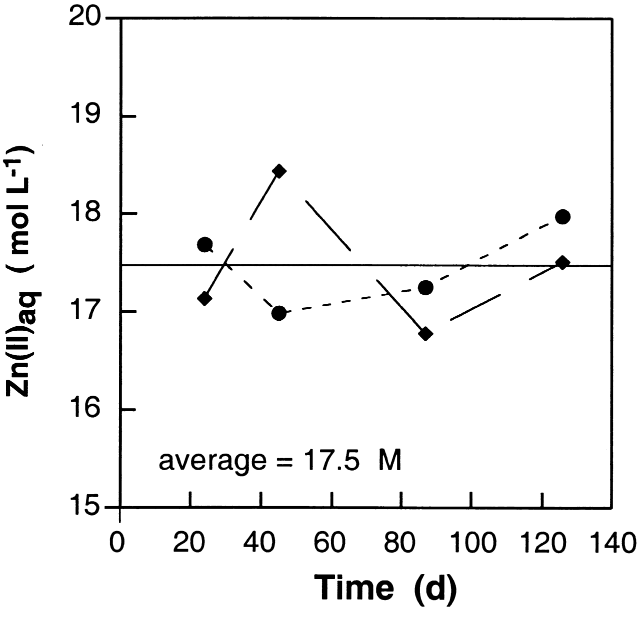

Fig. 1. Total dissolved Zn concentrations in equilibrium with Ca zincate of different size fractions as a function of time (pH = 11.75). Experiments were carried out with particle size fractions of < 100 μm (●) and >100 μm (◆).

Table 2
Stability constants used for the thermodynamic calculations $\{I = 0.1\ \mathrm{M}\}$

Equilibrium reaction	log*K*	Reference
Dissolved species		
$H_2O \Longleftrightarrow H^+OH^-$	− 13.78	[23]
$Zn^{2+} + H_2O \Longleftrightarrow ZnOH^+ + H^+$	− 9.18	[24]
$Zn^{2+} + 2H_2O \Longleftrightarrow Zn(OH)_2 + 2H^+$	− 17.12	[24]
$Zn^{2+} + 3H_2O \Longleftrightarrow Zn(OH)_3^- + 3H^+$	− 28.40	[24]
$Zn^{2+} + 4H_2O \Longleftrightarrow Zn(OH)_4^{2-} + 4H^+$	− 40.76	[24]
$Zn^{2+} + Cl^- \Longleftrightarrow ZnCl^+$	0.02	[25]
$Zn^{2+} + 2Cl^- \Longleftrightarrow Zn(Cl)_2$	− 0.07	[25]
$Ca^{2+} + H_2O \Longleftrightarrow CaOH^+ + H^+$	− 13.07	[24]
$Ca^{2+} + H_4SiO_4 \Longleftrightarrow CaH_2SiO_4 + 2H^+$	− 19.07	[23]
$Ca^{2+} + H_4SiO_4 \Longleftrightarrow CaH_3SiO_4^+ + H^+$	− 9.04	[23]
$H_4SiO_4 \Longleftrightarrow H_3SiO_4^- + H^+$	− 9.59	[26]
$H_4SiO_4 \Longleftrightarrow H_2SiO_4^{2-} + 2H^+$	− 22.48	[26]
$H_4SiO_4 + Na^+ \Longleftrightarrow NaH_3SiO_4 + H^+$	− 8.11	[27]
Solid phases		
$\beta_2\text{-}Zn(OH)_2Zn^{2+} + 2H_2O \Longleftrightarrow Zn(OH)_2 + 2H^+$	− 12.02	[28]
Calcium zincate $Ca^{2+} + 2Zn^{2+} + 6H_2O \Longleftrightarrow CaZn_2(OH)_6 + 6H^+$	− 44.56	This work

with the experimental conditions by using activity coefficients calculated using the Davies Equation.

3. Results and discussion

The aqueous total concentrations of Ca and Zn are shown as a function of pH in Fig. 2. The total dissolved Zn concentrations are between 10 and 200 μM, but the total Ca concentrations are much higher, between 300 and 17 000 μM. Zinc concentrations are relatively close to the calculated curve of total dissolved Zn content in equilibrium with $ZnO_{(s)}$. However, the measured Zn concentrations have a different relationship to pH than the calculated concentrations in equilibrium with ZnO (solid line in Fig. 2b). Measurements at the lowest pH values are about a factor of 2 larger than the ZnO solubility. With increasing pH, the difference diminishes; and around pH 12.5 the Zn concentrations become smaller than equilibrium with ZnO would allow. Dissolved Ca concentrations in equilibrium with calcium are between one and two orders of magnitude smaller than they would be in equilibrium with $Ca(OH)_{2(s)}$. In contrast to Zn, the aqueous Ca concentrations decrease with increasing pH. This decreasing solubility of the calcium hydroxides at high pH is due to the weak hydrolysis of Ca.

Calcium zincate appears to dissolve incongruently but the composition of the solid phase in our experiments does not change much. For most pH values, the calculated change in the Ca/Zn ratio of the solid phase is less than 1%, even after three sequential dissolution experiments. For the experiments at low pH, where dissolved Ca concentrations are high, it does not exceed 10%.

Because of the nearly constant solid phase composition, the following reaction is assumed to be valid for the calculation of the solubility of calcium zincate (Eq. (1)):

$$CaZn_2(OH)_6{\cdot}2H_2O_{(s)} + 6H^+_{(aq)} \leftrightarrow Ca^{2+}_{(aq)} + 2Zn^{2+}_{(aq)} + 8H_2O \qquad (1)$$

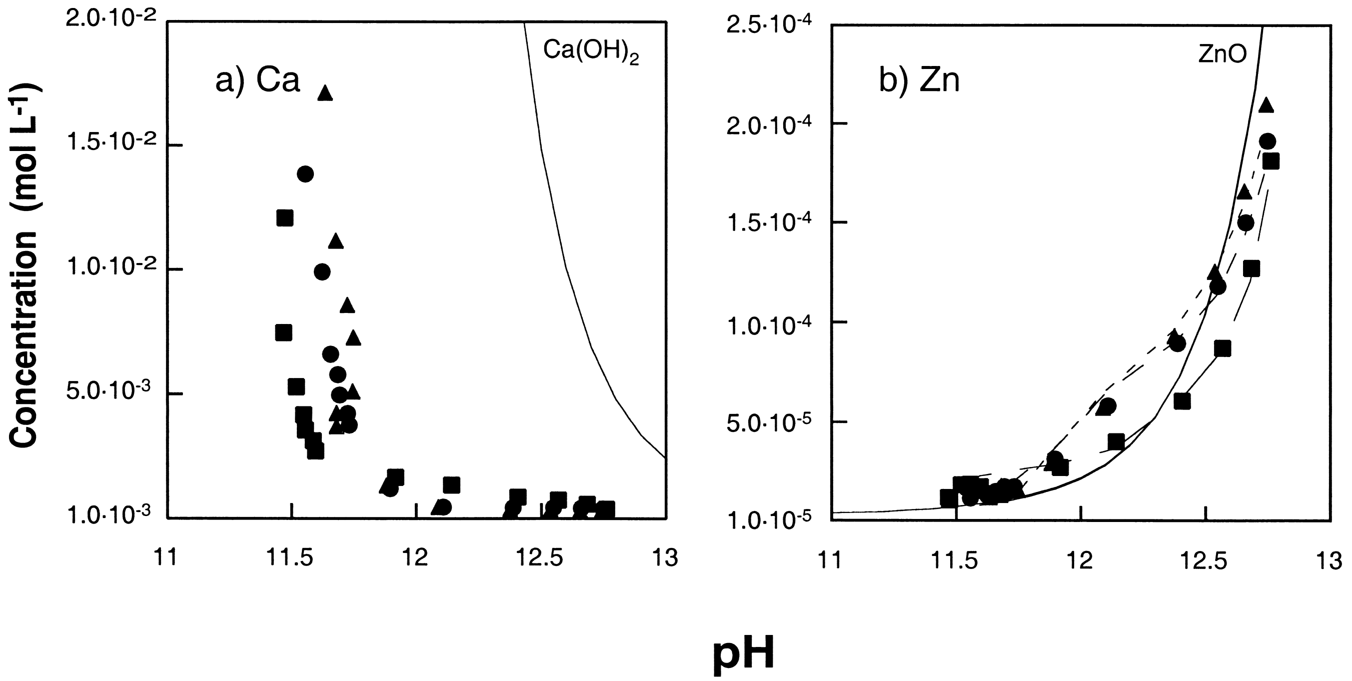

Fig. 2. Total dissolved concentrations of (a) Ca and (b) Zn in equilibrium with Ca zincate. The different solid symbols represent the results of sequential equilibrations with the same solid phase samples (■ 1st, ● 2nd, ▲ 3rd). The solid lines indicate the solubility in equilibrium with the appropriate (hydr)oxide phases. The dashed lines in (b) represent the solubility of Zn in equilibrium with Ca zincate using the solubility product estimated from the experimental data.

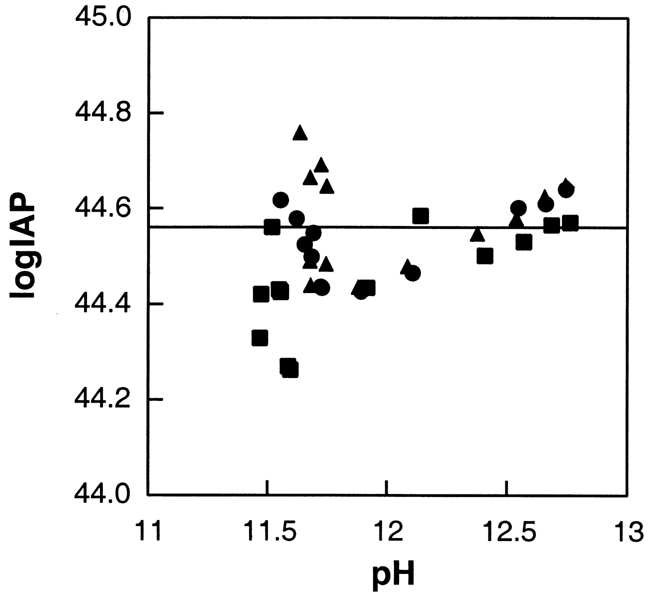

Fig. 3. The IAP in the solubility experiments with Ca zincate as a function of pH. The different symbols represent values obtained in sequential solubility experiments.

The equilibrium constant K_{s0} for this reaction is defined by (Eq. (2)):

$$\log K_{s0} = \frac{\{Zn^{2+}\}^2\{Ca^{2+}\}}{\{H^+\}^6} \tag{2}$$

where $\{Zn^{2+}\}$ and $\{Ca^{2+}\}$ are the activities of the free cation species in solution and $\{H^+\}$ is the aqueous proton activity. The activity of the solid phase is assumed to be unity.

The values of the ion activity product (IAP) on the right side of the equation were calculated for all experiments and plotted against pH (Fig. 3). The values had a narrow distribution. Although the Ca, Zn, and H^+ concentrations in the experiments can differ by a factor of 10 or more, the IAP was fairly constant. Hence, the data were fitted to the classical solubility constant using FITEQL 3 [19]. A value for $\log K_{s0}$ of 44.6 ± 0.7 was obtained. This value was valid for solutions at a constant ionic strength of 0.1 M. A correction for infinite diluted systems using the Davies coefficients gave a value of 43.9.

The fit was quite good. Also at low pH, where Ca was most soluble and we had the largest deviations of nearly 10% from the 2:1 ratio between Zn and Ca in the solid phase, the IAP from the experiments differed at most by a factor of 2 from the fitted K_{s0}. The solubility product was able to model the relation between aqueous Zn and Ca concentrations. As indicated in Fig. 2b by the dashed lines, calculations of the Zn concentrations with the fitted K_{s0} value and the appropriate Ca concentrations reproduced the experimental data quite well. The aqueous Zn concentrations in the sequential experiments could differ significantly at the same pH but were still in accordance with the solubility product.

A solubility constant for calcium zincate of $\log K_{s0} = 45.8$ (defined in the same way as above) has recently been published by Cocke et al. [10]. In order to compare the two values, it is assumed that the published value was calculated for a reference condition of infinite dilute solutions ($I = 0$ M), though this is not clear from the publication. The K_{s0} value of these authors is about two orders of magnitude larger than the value determined from the presented experiments. Thus, calculations with this constant appear to overestimate the Zn concentrations by approximately one order of magnitude at the same Ca and pH conditions.

Further evidence for the applicability of the determined solubility constant was given by sorption experiments of Zn to calcium silicate hydrate (C-S-H(I)) [13,14]. In these experiments, calcium zincate was precipitated at high Zn concentrations in experiments at pH 12.48 and 12.78, while at pH 11.7, β-$Zn(OH)_2$ precipitation was observed. A comparison between experimental data and model calculations (Fig. 4) showed good agreement and, in addition, was also able to explain the greater thermodynamic stability of Ca zincate above pH 12. For illustration, solubility curves for Zn in OPC cement pore water ([Ca] = 0.001 M, [SO_4] = 0.001 M, [Si] = 0.001 M, [Cl] = 0.2 M, I = 0.5 M [20]) adjusted using Pitzer according to Millero et al. [21,22] were also shown in Fig. 4. These calculations illustrated the thermodynamic stability of Ca zincate above pH 12 in the absence of other Zn interactions.

However, because of the incongruent dissolution of calcium zincate, the fitted solubility constant cannot be used without limitations.

1. The solubility product is not able to model both the Zn and Ca concentration at a given pH value. One of the free aqueous concentrations (Ca^{2+} or Zn^{2+}) must be given for the calculation of the other.

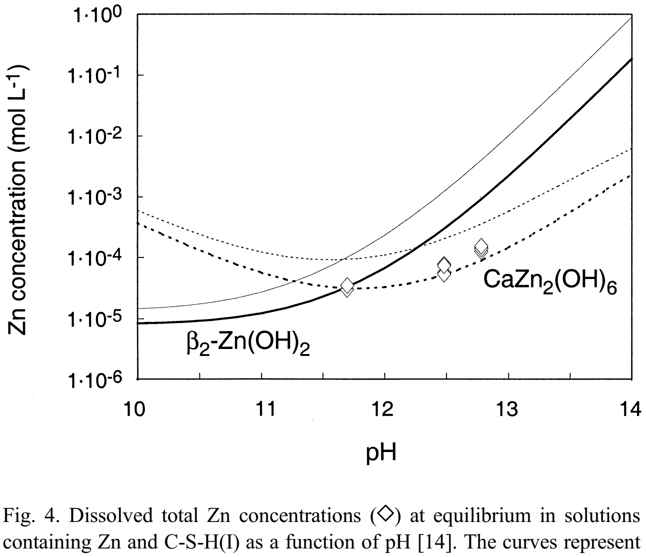

Fig. 4. Dissolved total Zn concentrations (◇) at equilibrium in solutions containing Zn and C-S-H(I) as a function of pH [14]. The curves represent the calculated solubilities of Zn at equilibrium with Ca zincate and β_2-$Zn(OH)_2$ for the experimental conditions (thick lines) and for cement pore water (thin lines).

2. The solubility product is only applicable for a narrow range of compositions of the calcium zincate around a Zn/Ca ratio of 2.

An explanation for the apparent incongruent dissolution could be the presence of mineral impurities such as ZnO or $Ca(OH)_2$ in the solid phase. But there are some arguments against such an objection. Firstly, the XRPD spectra of the solid phase do not show any impurities before and after the experiments, the calcium zincate is the only detectable phase. Although the detection limit for a crystalline solid phase in XRPD is at about 5%, a possible Ca impurity, e.g., $Ca(OH)_2$, should be visible at least at low pH, where the highest amounts of dissolved Ca are larger than 5%. Secondly, the aqueous Ca concentrations at low pH (where the highest Ca concentrations occur) do not diminish with the sequence of experiments, as one can expect for an impurity. And thirdly, the aqueous Ca and Zn concentrations are not independent. The relation between these concentrations can be modeled by the application of the solubility product.

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