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Thermodynamic data for the solubility of tin(IV) in aqueous cementitious environments

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Summary. The solubility of Sn(IV) in cementitious systems is directly related to the presence of dissolved Ca. In the presence of typical Ca concentrations, solid $Ca[Sn(OH)_6]$ (s) is precipitated, resulting in dissolved tin(IV) concentrations that are about four to six orders of magnitude lower than observed in alkaline, Ca-free systems. From different experiments carried out in initially oversaturated and undersaturated solutions, solubility products have been evaluated.

A constant of $10^{9.85}$ at $I = 0$ has been derived for the formation of fresh $Ca[Sn(OH)_6]$ (precip) according to the reaction $Ca^{2+} + Sn(OH)_6{}^{2-} \Leftrightarrow Ca[Sn(OH)_6](s)$. A constant of $10^{10.93}$ has been derived in undersaturation experiments for the equilibrium with crystalline $Ca[Sn(OH)_6]$ (cr).

Introduction

The solubility of radionuclides under conditions relevant for nuclear waste repositories is an important parameter for safety analysis. For tin(IV), little is known about its chemistry under the alkaline conditions expected in the near-field of a repository containing cement-based material. Little quantitative information exists in general on the solubility of solid Sn(IV) phases and the hydrolysis of Sn(IV). Using the sparse thermodynamic data for Sn(IV) as e.g. compiled in [1] or [2], Sn concentrations ≥ 0.01 M would be possible at pH 12 and above. Recently, a systematic experimental study has been published [3], which investigates the solubility of crystalline SnO_2(cassiterite) and poorly crystalline $SnO_2 \times xH_2O$,(precipitated) in $NaClO_4$ electrolyte. At pH 12, Sn concentrations in the range of 0.01 M were reported.

However, in a previous paper [4], we could show that in cementitious environments, the solubility of tin(IV) might be drastically lower. Here, we demonstrate that the solubility of Sn(IV) in cementitious systems is directly related to the presence of dissolved Ca. Solid $Ca[Sn(OH)_6]$(s) is precipitated, resulting in dissolved tin(IV) concentrations that are significantly lower than observed in corresponding Ca-free systems.

In order to set realistic upper limits for the solubility of tin a number of experiments have been carried out (i) to confirm $Ca[Sn(OH)_6]$(s) as the solubility limiting solid in cementitious systems and (ii) to measure its solubility in such systems. The solubility of $Ca[Sn(OH)_6]$(s) was approached in solutions containing 0.25, 0.5 or 2.0 M $NaClO_4$ as inert electrolyte from both under- and oversaturation in the pH range 11 to 13.1.

Materials and methods

Experimental approach

Experiments under alkaline conditions were generally carried out at 25 °C in 100 mL polyethylene terephtalate co-polyester (PETG) vessels. PETG vessels were used to avoid the slow dissolution of silica from glass vessels under highly alkaline conditions. PETG is chemically inert and has a very low permeability for CO_2 in comparison to other plastics (e.g. polyethylene). The batch vessels are purged with argon to exclude CO_2 during the addition of the chemicals, closed tightly and shaken at 80 rpm at 25 °C. The argon gas was stripped of CO_2 by bubbling it through 0.1 M NaOH solutions. After equilibration time, the OH^- concentration was measured under argon and an aliquot of the suspension was taken to determine the Ca and Sn concentrations. Ca was measured by flame-atomic absorption spectrometry and Sn by graphite furnace-atomic absorption spectrometry using a NH_3/Pd/ascorbic acid modifier. Phase separation was generally done by filtration through 0.45 μm membrane filters; for comparison some samples (under different pH conditions, [Ca] and [Sn] concentrations) were filtrated by 0.02 μm membrane filters or 10 000 MWCO polysulfone membrane filters. No significant difference in the measured Sn concentrations was observed. Previous to the experiments, some additional batch experiments were set up to monitor Sn solubility as a function of time. Measured $[OH^-]$ remained constant during the whole time of the experiments. Constant Sn concentrations were reached within one to seven days in solutions where $Ca[Sn(OH)_6]$ (precip) was precipitated (Fig. 1a), while in solutions above $Ca[Sn(OH)_6]$ (cr) equilibrium was reached after approx. 2 months (Fig. 1b).

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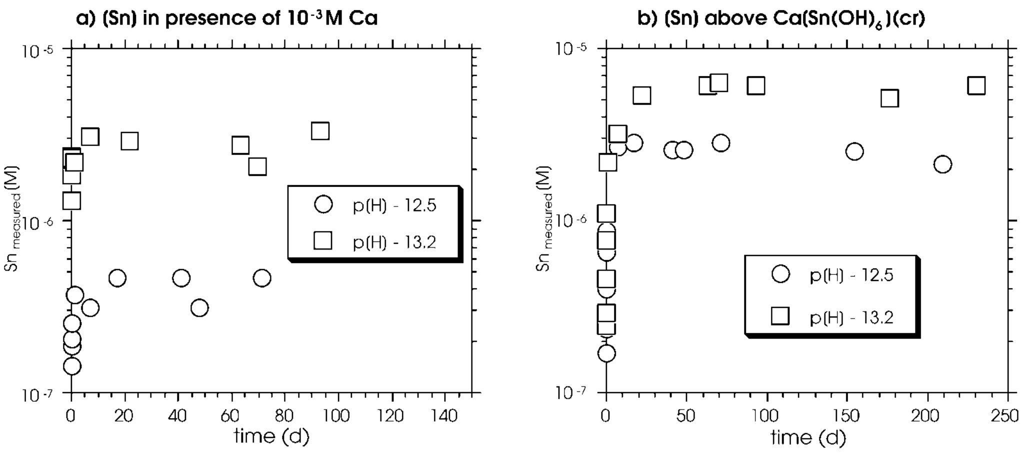

Fig. 1. Measured Sn concentrations at $I = 0.5$ M $NaClO_4$ as a function of time at p[H] 12.5 and 13.2 (**a**) in solutions containing 1.3×10^{-5} M Sn, 1×10^{-3} M Ca, (**b**) above $Ca[Sn(OH)_6]$ (cr). Phase separation is done by filtration (0.45 µm).

In this paper, the notation p[H] is used to indicate a concentration, while pH refers to H^+ activities. The p[H] – or rather the $[OH^-]$ concentration – was determined with a Metrohm 6.0204.100 combined electrode and a Metrohm 654 pH-meter. Calibration was carried out with acid-base titration in the $[OH^-]$ range of 0.001 to 0.1 M and in the respective ionic media. During $[OH^-]$ calibration the vessels were purged with argon and the mV readings (E′) were recorded when the drift was < 0.5 mV/min. The E′ readings were corrected for the difference in the diffusion potential caused by the increasing fraction of OH^- ions present under highly alkaline conditions.

Preparation of $Ca[Sn(OH)_6]$ (cr)

About 7 g of $SnCl_4 \times 5H_2O$ (s) were diluted in approx. 800 mL of bidistilled water and 7 g NaOH (s) were added, resulting in a clear solution with a p[H] value of ≈ 12.5. Upon addition of 6 g $Ca(ClO_4)_2 \times 4H_2O$ (s) a white precipitate formed. The precipitate was allowed to settle and the clear solution was removed. The precipitate was resuspended twice in bidistilled water to remove excess Na, Cl and ClO_4 and dried at 40 °C. The XRD pattern of the white powder matches the pattern given by [5] for $Ca[Sn(OH)_6]$ (cr).

Oversaturation experiments

Bidistilled water, $NaClO_4$, $SnCl_4$, $Ca(ClO_4)_2$ and NaOH were added to PETG vessels to achieve the intended Sn and Ca concentrations and an ionic strength of 0.25, 0.5 and 2.0 M respectively. Ca concentrations ranged from 2×10^{-5}–2×10^{-2} M, Sn concentrations from 1×10^{-7}–1×10^{-4} M and p[H] was 12.5 or 13.1. OH^-, Sn and Ca concentrations were determined after one week.

Undersaturation experiments

$Ca[Sn(OH)_6]$ (cr) was equilibrated with solutions containing the appropriate amount of bidistilled water, $NaClO_4$, and NaOH to obtain an ionic strength of 0.25, 0.5 and 2.0 M, respectively, and pH values in the range 11.1 to 13.1. OH^-, Sn and Ca concentrations were determined after two and four months.

Calculational tools and thermodynamic data

For the calculation of speciation and fitting the program GRFIT [6] was used, which is based on the well-known code FITEQL [7]. Both codes use a non-linear, least-squares optimization technique to calculate equilibrium constants from chemical data. Thermodynamic data for Ca and Na hydrolysis are taken from [8], while the data for Sn hydrolysis are based on the solubility measurements of [3] as corrected to $I = 0$ by [9] with the SIT approach. Extrapolation of the calculated thermodynamic data for $Ca[Sn(OH)_6]$ (s) to $I = 0$ was done using the specific ion interaction equation (SIT) as given in [10]. An extensive description of SIT and its use can be found in Appendix B of [10] and [11].

Results

Precipitation from oversaturated solutions

Sn and Ca concentrations were varied systematically in solutions containing $NaClO_4$ as supporting electrolyte at p[H] values of 12.5 and 13.1. The resulting Sn and Ca concentrations as a function of the amount of Ca or Sn initially added are given in Fig. 2. Figs. 2a–c show the influence of increasing [Ca] on measured Sn concentrations. The measured Sn concentrations remain constant at $\approx 10^{-5}$ M, which shows that no precipitation occurs until a Ca concentration of $\approx 10^{-3}$ M is reached (Fig. 2a). Upon addition of higher Ca concentrations, Sn concentrations decrease linearly as function of increasing Ca concentrations, indicating the precipitation of a solid phase (Figs. 2a and 2b). A linear decrease of measured Sn concentrations as a function of increasing [Ca] is also observed in Fig. 2c using higher initial Sn concentrations ($\approx 10^{-5}$ M). Experiments, which show the influence of increasing Sn concentrations on measured [Ca] and [Sn] are shown in Figs. 2d and 2e. The increase of [Sninit] in the presence of 10^{-3} M Ca, resulted in increasing measured Sn concentrations until a Sn concentration of $\approx 3 \times 10^{-6}$ M was reached (Fig. 2d). Upon addition of higher $[Sn_{init}]$, Sn concentrations of approx. 3×10^{-6} M were measured in presence of $Ca[Sn(OH)_6]$ (precip).

The Ca and Sn concentrations measured in different batch experiments and the thermodynamic data given in Table 1 were used to fit a solubility product for the for-

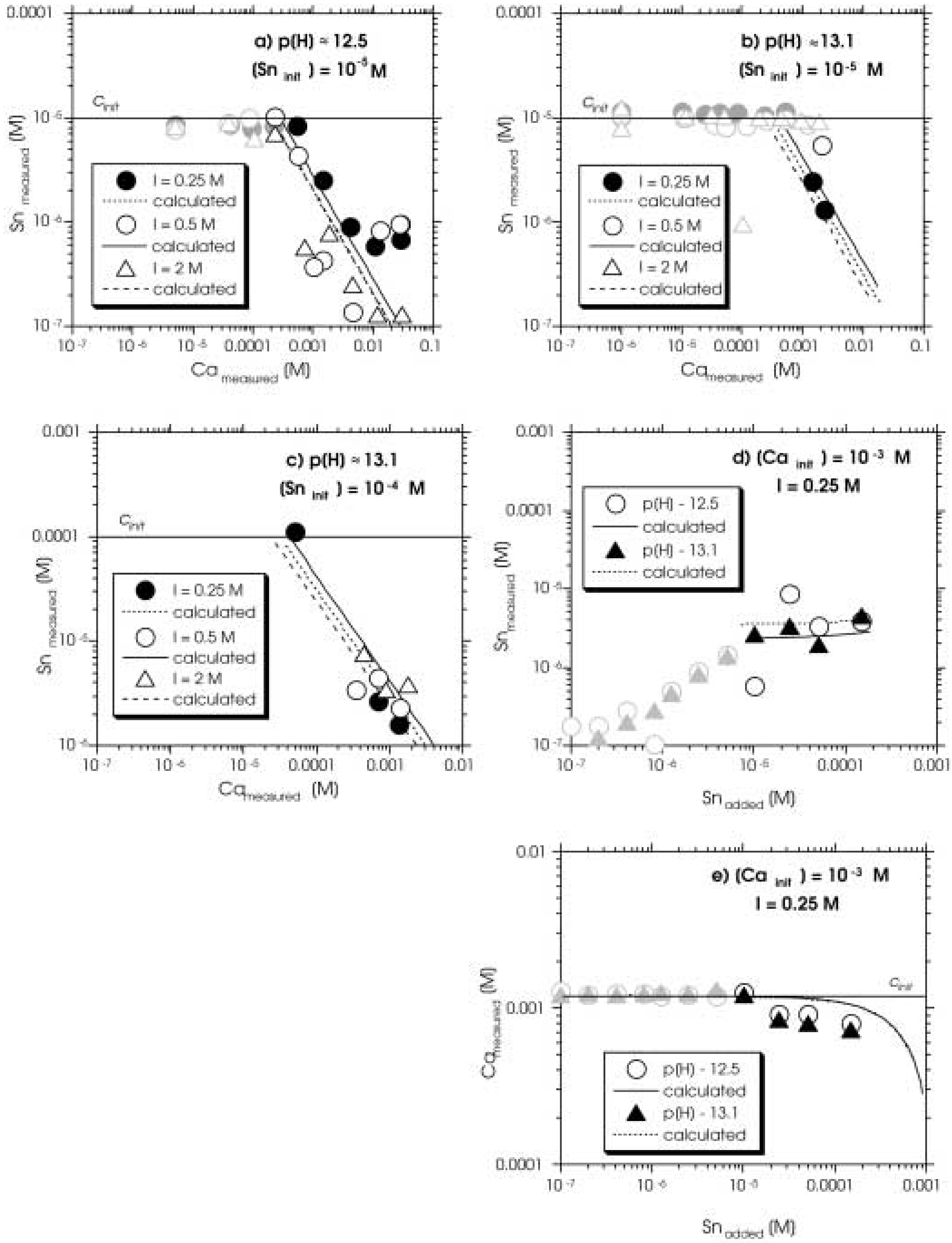

Fig. 2. Measured Sn concentrations as a function of [Ca] concentration in sodium perchlorate medium after 1 week; (**a**) p[H] ≈ 12.5, initial Sn concentration 1×10^{-5} M, (**b**) p[H] ≈ 13.1, initial Sn concentration 1×10^{-5} M, (**c**) p[H] ≈ 13.1, initial Sn concentration 1×10^{-4} M, (**d**) initial Ca concentration 1×10^{-3} M, $I = 0.25$ M, (**e**) Ca concentrations as a function of the amount of Sn initially added. Ca concentration 1×10^{-3} M, $I = 0.25$. Phase separation is done by filtration (0.45 µm).

Table 1. Overview over the thermodynamic data (log hydrolysis constants and solubility products) used.

	Species/Solids	Constants	Source
Dissolved species			
$Ca^{2+} + H_2O$	$\Leftrightarrow CaOH^+ + H^+$	$\log K^\circ_{1,1} = -12.85$	[8]
$Na^+ + H_2O$	$\Leftrightarrow NaOH^0 + H^+$	$\log K^\circ_{1,1} = -14.18$	[8]
$Sn(OH)_4{}^0 + H_2O$	$\Leftrightarrow Sn(OH)_5{}^- + H^+$	$\log \beta^\circ_{1,5} = -7.97$	[8]
$Sn(OH)_4{}^0 + H_2O$	$\Leftrightarrow Sn(OH)_6{}^{2-} + 2H^+$	$\log \beta^\circ_{1,6} = -18.40$	[9]
Solid species			
$Sn(OH)_4{}^0$	$\Leftrightarrow SnO_2$ (cassiterite) $+ 2H_2O$	$\log K^\circ_{S4} = 8.05$	[9]
$Sn(OH)_4{}^0$	$\Leftrightarrow SnO_2$ (precip) $+ 2H_2O$	$\log K^\circ_{S4} = 7.46$	[9]
$Sn(OH)_4{}^0 + Ca^{2+} + 2H_2O$	$\Leftrightarrow Ca[Sn(OH)_6]$ (cr) $+ 2H^+$	$\log K^\circ_{S6} = -7.47$	this paper
$Sn(OH)_4{}^0 + Ca^{2+} + 2H_2O$	$\Leftrightarrow Ca[Sn(OH)_6]$ (precip) $+ 2H^+$	$\log K^\circ_{S6} = -8.55$	this paper

Table 2. Individual solubility products for $Ca[Sn(OH)_6]$ (precip) in solutions containing 0.25, 0.5 or 2 M $NaClO_4$ as obtained in oversaturated solutions.

I [M]	p[H]	variation of	$\log K^*_{S6}$
0.25	12.5	Ca	−8.44
0.25	13.1	Ca	−8.60
0.5	12.5	Ca	−8.51
0.5	12.5	Sn	−8.71
0.5	13.1	Ca	−8.82
0.5	13.1	Sn	−8.89
2.0	12.5	Ca	−8.84
2.0	13.1	Ca	−8.49

mation of $Ca[Sn(OH)_6]$ (precip). In Fig. 2, the data used for deriving the formation constants are shown in black, while all other data are shown in gray. A compilation of the results at different ionic strength, pH values and variation of Ca or Sn is given in Table 2. Solubility products of $Ca[Sn(OH)_6]$ (precip) obtained in the individual experimental series (Table 2) show a slight decrease with increasing ionic strength. The constants obtained for each ionic strength were extrapolated to $I = 0$ using the SIT approach [10, 11], resulting in:

$$Ca[Sn(OH)_6]\ (precip) \Leftrightarrow Sn(OH)_6{}^{2-} + Ca^{2+}$$
$$\log K^\circ_{S6} = -9.85$$

or, using the thermodynamic data as compiled in Table 1:

$$Ca[Sn(OH)_6]\ (precip) + 2H^+ \Leftrightarrow$$
$$Sn(OH)_4{}^0 + Ca^{2+} + 2H_2O \quad \log K^\circ_{S4} = 8.55$$

Dissolution of $Ca[Sn(OH)_6]$ (cr) in undersaturated solutions

In solutions initially undersaturated with respect to $Ca[Sn(OH)_6]$ (cr), an excess of solid $Ca[Sn(OH)_6]$ (cr) was allowed to dissolve and the concentrations of OH^-, Sn and Ca were determined in the p[H] range 11.1 to 13.1 after an equilibration time of two and four months. The measured concentrations of Sn above $Ca[Sn(OH)_6]$ (cr) at $I = 0.25$, 0.5 and 2 M are given in Fig. 3. It can be seen that in a large number of experiments equilibrium had not yet been reached after 2 months. After 4 months, however, most suspensions seem to have reached equilibrium. It also appears that dissolution kinetics is faster at higher OH^- concentrations.

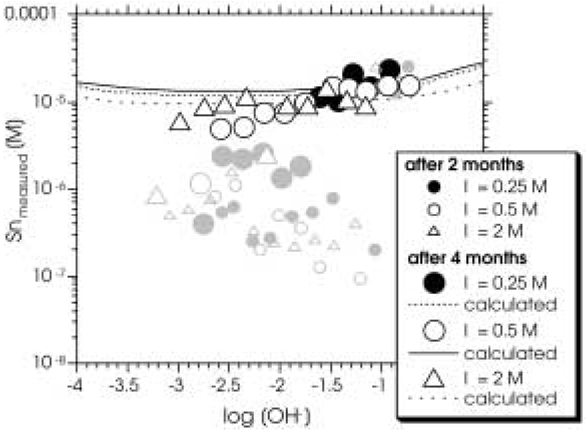

Fig. 3. Sn concentrations above $Ca[Sn(OH)_6]$ (cr) as a function of $[OH^-]$ in sodium perchlorate solutions. Phase separation: filtration (0.45 μm).

Table 3. Individual solubility products for $Ca[Sn(OH)_6]$ (cr) in solutions containing 0.25, 0.5 or 2 M $NaClO_4$ as obtained in undersaturated solutions.

I [M]	p[H] range	$\log K^*_{S6}$ [Ca] = [Sn]
0.25	12.0 − 13.1	−9.67
0.5	11.5 − 13.1	−9.99
2.0	11.1 − 13.1	−10.02

For the calculations of formation constants, only values determined after 4 months have been used and any value that was significantly lower than the others has been excluded, as in some cases equilibrium may not yet have been reached. The constants obtained for each ionic strength (Table 3) were again extrapolated to $I = 0$ using the SIT approach:

$$Ca[Sn(OH)_6]\ (cr) \Leftrightarrow Sn(OH)_6{}^{2-} + Ca^{2+}$$
$$\log K^\circ_{S6} = -10.93$$

or, using the thermodynamic data compiled in Table 1:

$$Ca[Sn(OH)_6]\ (cr) + 2H^+ \Leftrightarrow Sn(OH)_4{}^0 + Ca^{2+} + 2H_2O$$
$$\log K^\circ_{S4} = 7.47$$

The solubility product calculated for $Ca[Sn(OH)_6]$ (precip) is approximately one log unit higher than the solubility product of $Ca[Sn(OH)_6]$ (cr). The drying of $Ca[Sn(OH)_6]$ (precip) has presumably increased the crystallinity of calcium stannate and decreased its solubility.

Identification of the solid phases by X-ray diffraction

Solid $Ca[Sn(OH)_6]$ (cr) that was aged for 80 days in 0.25 M $NaClO_4$ solutions at p[H] 12.1 and 13.1 and $Ca[Sn(OH)_6]$ (precip) that has precipitated from oversaturated solutions at pH 12.5 and 13.1, have been dried at 40 °C and analyzed by X-ray diffraction measurements. No difference was observed between the different p[H] values and whether the solids have already been dried previously (as in the undersaturation experiments). Thus, under all experimental conditions the same solid has precipitated. The difference in solubility observed in over- and undersaturation experiments is because the solids used in the undersaturation experiments have been dried prior to its use, which led presumably to the formation of a more crystalline structure. The solids precipitated in the oversaturation experiments are more amorphous and crystallize during drying.

Calculated solubility limits and speciation

The speciation of Sn and the solubility-determining phase under a range of pH conditions and different Ca con-

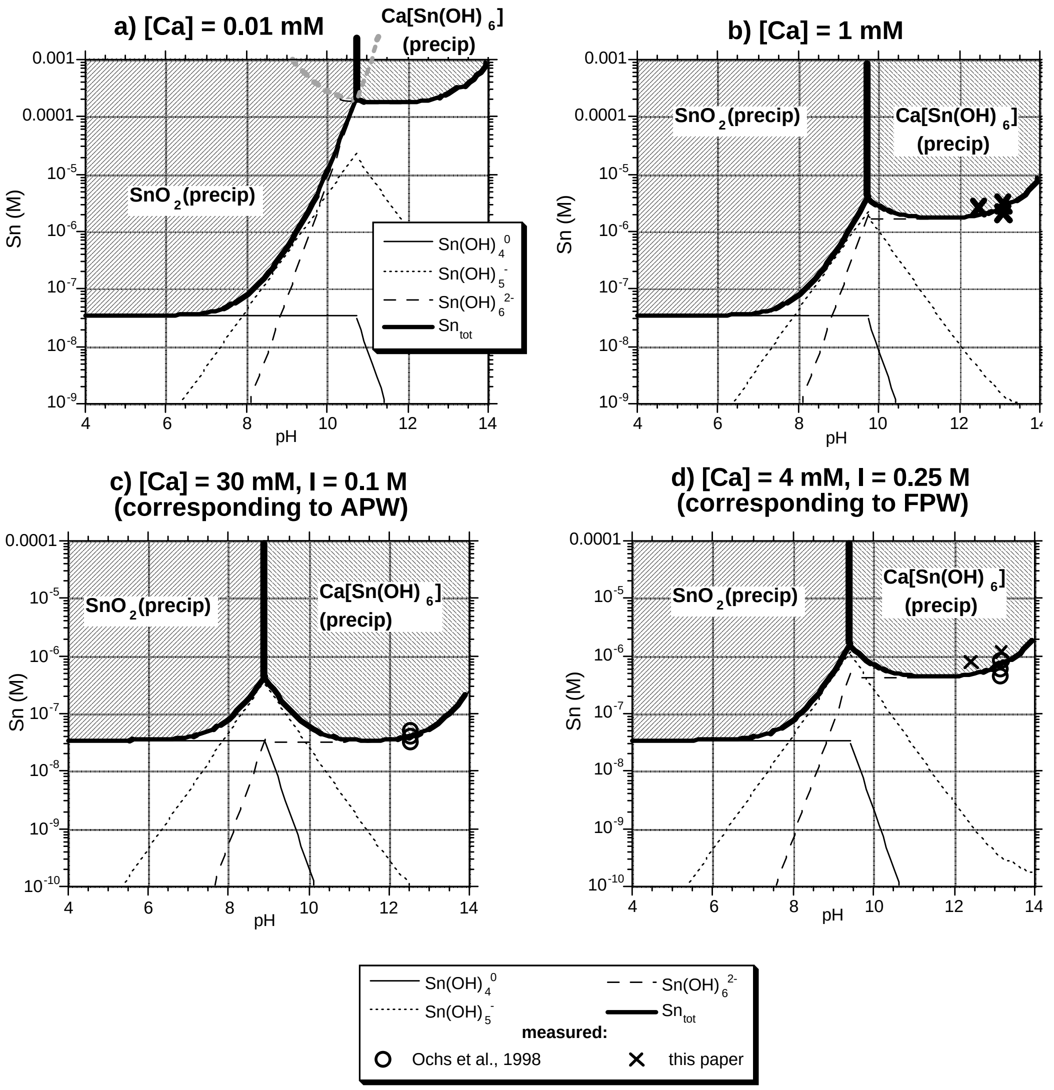

Fig. 4. Calculated Sn speciation and solubility as a function of pH and Ca concentration at (**a**) [Ca] = 0.01 mM, $I = 0.25$ M, (**b**) [Ca] = 1 mM, $I = 0.25$ M (Values measured in this paper have been added for comparison), (**c**) [Ca] = 30 mM, $I \approx 0.1$ corresponding to aged cement porewater (APW) [4], measured [Sn] from [4], (**d**) [Ca] = 4 mM, $I \approx 0.25$ corresponding to fresh cement porewater (FPW) [4], measured [Sn] from [4] or measured in solutions containing 4 mM Ca at $I = 0.25$ M (this paper). Calculated using the solubility product of $Ca[Sn(OH)_6]$ (precip) determined in this paper and the thermodynamic data from Table 1.

centrations has been calculated with the program GRFIT using the thermodynamic data compiled in Table 1. All calculations were carried out considering SnO_2 (precip) and $Ca[Sn(OH)_6]$ (precip) as the solubility limiting phase. Solid tin oxides/hydroxides of different crystallinity may be formed in solutions. Cassiterite only crystallizes at elevated temperatures (≈ 300 °C), while at lower temperature precipitates are less crystalline [12]. SnO_2(cassiterite) is thus not expected to precipitate under natural or repository conditions. Freshly precipitated Sn(IV) hydroxides, $Sn(OH)_4$ (am), are reported to be amorphous and easily soluble. However, such a solid will turn into a poorly crystalline SnO_2 (precip) within a short time of aging [3, 13]. $Ca[Sn(OH)_6]$ (precip) precipitates from oversaturated solutions while during drying at 40 °C the more crystalline $Ca[Sn(OH)_6]$ (cr) is formed.

Dissolved Sn concentrations as a function of [Ca] and pH

Fig. 4 illustrates that in the pH range 4 to 10.7 and in the presence of 10^{-5} M Ca, Sn(IV) solubility is limited by the precipitation of SnO_2 (precip). At higher pH values, $Ca[Sn(OH)_6]$ (precip) controls the dissolved Sn concentrations. In the presence of higher Ca concentrations, the pH range where $Ca[Sn(OH)_6]$ (precip) determinates Sn(IV) solubility extends to lower values and the Sn solubility under alkaline conditions decreases (Fig. 4). In the presence of 0.01 mM Ca, $\approx 10^{-4}$ M Sn will be dissolved in the pH range $11-13.5$, while only 10^{-7} M Sn are expected to be dissolved in the presence of 10 mM Ca. Thus, under alkaline conditions, Sn concentrations are mainly determined by the concentration of Ca. In the absence of Ca, Sn concentrations increase strongly with increasing p[H] (cf. dotted line in Fig. 4a).

Tin solubility as a function of pH has also been calculated using Ca concentrations and ionic strength conditions as they can be expected in fresh and in aged cement porewaters (Figs. 4c and 4d). Sn solubilities measured in cement porewaters in a previous study [4] agree very well with the Sn solubility predicted from the thermodynamic data given in Table 1 (Figs. 4c and 4d). Thus, the thermodynamic data obtained from the well-defined systems used in the present investigations are able to predict Sn concentrations measured in much more complex, real cement porewaters. Similar Sn solubilities, 10^{-7}–10^{-5} M, have been measured by Bayliss *et al*. [14, 15] in the presence of cement equilibrated water. However, it was not possible to recalculate these experiments as the final Ca concentrations have not been determined in [14] and [15].

Conclusions and outlook

The presence of dissolved Ca determinates the solubility of Sn(IV) under alkaline conditions. X-ray diffraction measurements identified $Ca[Sn(OH)_6](s)$ as the solubility limiting solid. These findings illustrate the difficulties to predict the solubility of radioelements in the near-field of a repository containing cement-based material. For a number of elements, anionic species are formed under such high pH conditions, which may form stable precipitates with cations, i.e. Ca, present in cementitious environments.

Recently, it has been observed, that similarly to Sn(IV), Nb(V) solubility is drastically reduced in the presence of Ca under alkaline conditions. Measured Nb concentrations were reduced at $pH \approx 12.3$ upon the addition of 30 mM Ca from 1×10^{-3} M to less than 5×10^{-8} M Nb. XRD measurements identified the precipitate as $CaNb_2O_6 \times nH_2O$ [16].

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