SOLUBILITY AND MOBILITY OF PB-BEARING SPECIES UNDER CANDU STEAM GENERATOR CONDITIONS

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ABSTRACT

As part of a coordinated program, AECL is developing a set of tools to aid with the prediction and management of steam generator (SG) performance. One important mode of degradation within SGs is intergranular and transgranular stress corrosion cracking (SCC) of SG tubing. Numerous and extensive laboratory studies have demonstrated a definite link between lead and SCC. The prediction of the SG degradation is hindered by the lack of reliable thermodynamic data on the solubilities of lead compounds under SG operating conditions.

For lead induced SCC to occur, lead needs to be transported to the metal-oxide interface on the SG tube. AECL has been developing a model to predict such a transport of lead towards (or away from) the metal interface. If the direction of the lead transport can be predicted as a function of water chemistry conditions, practical means of dealing with SG contamination with Pb could be devised and Pb-SCC could be mitigated by appropriate adjustment of the water chemistry. The solubilities for the relevant Pb-bearing species under SG operating conditions are necessary for the application of this model. However, the lack of reliable thermodynamic data make it difficult to calculate the solubilities of lead compounds in typical SG under-deposit environments.

In this paper, the experimental method used for the determination of Pb solubility is presented and the preliminary experimental results for lead sulphate are given as a function of temperature and ionic strength under the range of conditions relevant to CANDU SGs.

1. Introduction

The presence of lead (Pb) can contribute to intergranular and transgranular stress corrosion cracking (SCC) of steam generator (SG) tubing, which was first reported in 1965 [1]. Since then, lead-induced SCC of SG tubing materials has been found extensively in both laboratory studies and in nuclear power stations [2]. Although the detailed mechanism of lead-induced SCC is not well understood, lead was identified as the cause of transgranular cracking and leaking of SG tubes of Unit 2 of Bruce A Nuclear Generating Station (BNGS) [3]. The introduction of lead blankets to one of the SGs of BNGS in 1986 exacerbated SCC and eventually resulted in the shutdown of Unit 2 in 1995 September [4].

Lead can enter the SGs from lead-containing materials around the secondary circuits, including pump seals, bushings, lead billets, valve packings, paints, coatings, pipe thread sealants and lubricants, liners, etc. Turbines represent a great potential source of lead contamination in feedwater, because the clearance between the turbine rotor and stator is measured by crushing lead wires [5]. Pieces of these wires can drop into the turbine after each operation. Lead masses wrapped in plastic used in turbine maintenance may also contribute to contamination. The lead content[1] in carbon and stainless steel varies between 1 and 10 mg/kg and that in copper alloys is around 100 mg/kg. Hence, the feedwater components provide a minor source of lead contamination. However, some types of carbon steel, not normally used for feed train components, may contain up to 0.35 mass % of lead. Chemicals used for pH control could also add lead to the system, e.g., an impurity concentration of 1 mg Pb/kg of morpholine could introduce 10 g of Pb per year.

Lead species from various sources can be transported by the feedwater and deposited inside the SGs. A relatively large amount of lead has been found in the deposits of the secondary side of SGs. The typical lead concentration in the sludge ranges from 0.02% to 0.2% (200 to 2000 mg/kg), while the concentration of dissolved lead in the feedwater is at ppt levels.

As part of a coordinated program, AECL is developing a set of tools to aid with the prediction and management of SG performance. The prediction of the SG degradation is hindered by the lack of reliable thermodynamic data on the solubilities of lead compounds under SG operating conditions. Recently, a refreshed autoclave system was commissioned to measure the high temperature solubilities of relevant lead compounds under CANDU SG conditions. From these data, the dominant dissolved lead species under SG feedwater chemistry and the possible key lead compound(s) inducing SCC in SG tubing, can be determined and be used to develop a model to predict lead transport in SGs.

The relevant impurities in the feed water are typically Cl^-, SO_4^{2-}, SiO_2, Fe^{2+}/Fe^{3+}, Ca^{2+}, Mg^{2+}, Na^+, and Al^{3+}. These impurities can become highly enriched in crevice environments as the solution continuously boils and will precipitate once the concentrations exceed the corresponding solubilities of specific components. The pH of the crevice solutions can be alkaline or acidic determined by the ionic composition of the solution in equilibrium with the precipitates. The impurities in the feed water, and especially in crevices, can significantly change the solubility of lead compounds in the SGs because of common ion effect, ionic strength, complexation, etc.

In this paper, the experimental methods used for the determination of solubility of the Pb compounds are discussed and the preliminary experimental results of the solubility $PbSO_4$ in water and NaCl solutions as a function of temperature are presented.

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[1] In a solution of mononuclear lead species, 1 µg/kg = 4.826×10^{-9} *mol/kg*.

2. Literature Review of Solubility of Lead Sulphate

The earliest solubility data for $PbSO_4$ were reported in 1903 [6], which gave a value of 1.34×10^{-4} mol/kg at 25°C. Clever and Johnston [7] reviewed the solubility data of $PbSO_4$ in aqueous solutions and recommended the value of $(1.46\pm0.04) \times 10^{-4}$ mol/kg. The solubility product (K_{sp}) of $PbSO_4$ recommended by Smith and Martell [8] was 1.62×10^{-8} at 25°C while a tentative K_{sp} value 2.53×10^{-8} at 25°C was recommended by Clever and Johnson [7].

Experimental solubility data for $PbSO_4$ from room temperature to 50°C was reviewed by Clever and Johnson [7] and their data show that the solubility of $PbSO_4$ in water increases roughly linearly with increasing temperature (Figure 1) over this range.

There is little solubility data for $PbSO_4$ above 50°C and only two experimental points at 60°C have been reported [9], [10] shown on Figure 1. The results suggest that the solubility of $PbSO_4$ reaches a maximum at around 50°C.

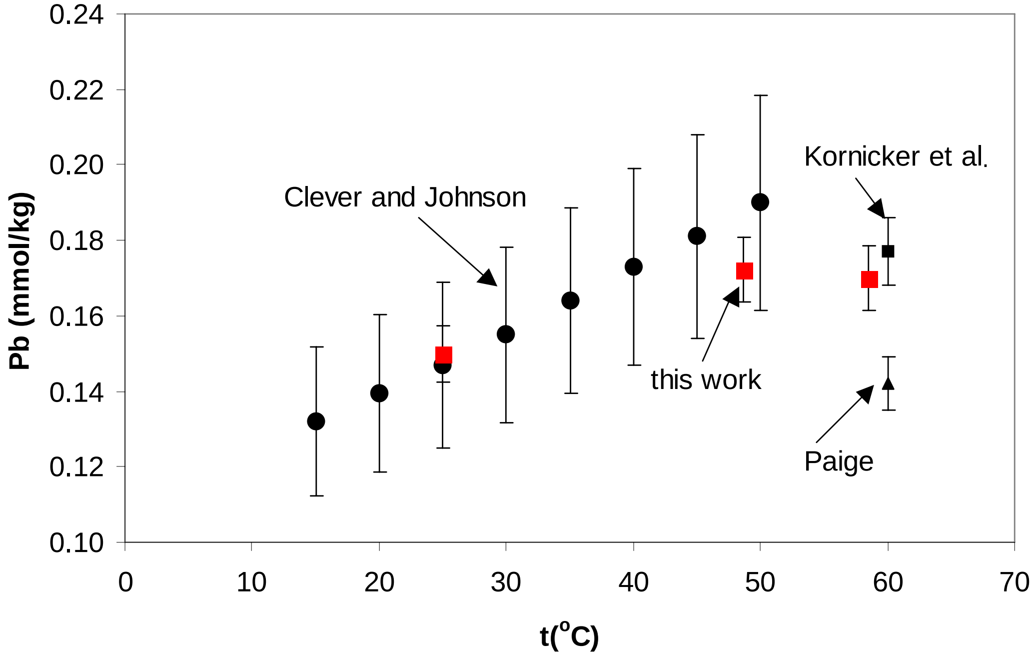

Figure 1 Solubility of $PbSO_4$ in water below 60°C.

The solubility product of $PbSO_4$ from 25 to 300°C was calculated by Helgeson [11] and Khodakovskiy [12] using empirical methods which estimated heat capacities of lead species at high temperatures from those at room temperature. The solubilities of lead sulphate from these K_{sp} calculations show maxima at 60°C and 100°C, respectively. However, in the absence of experimental data, it is not possible to determine which of these two calculations to use.

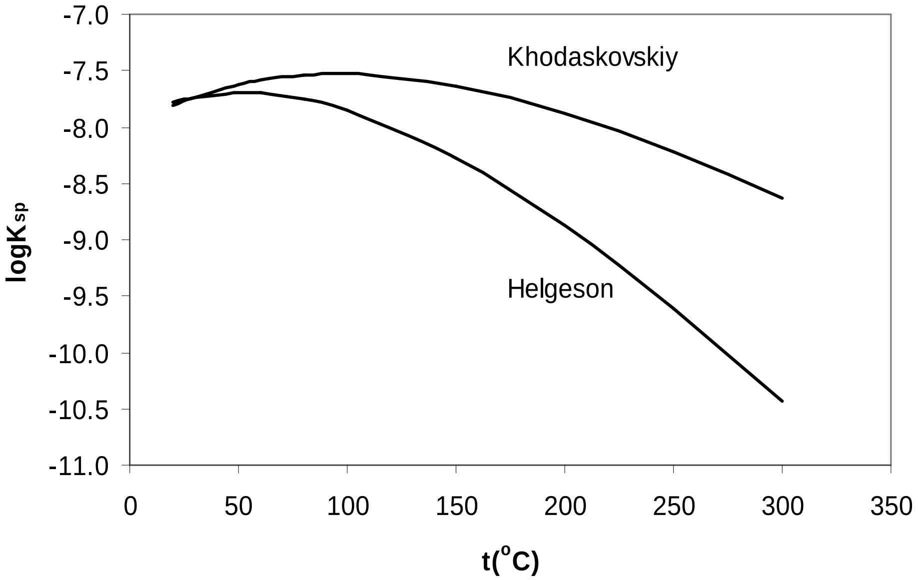

Figure 2 Calculated $PbSO_4$ K_{sp} values of Helgeson [11] and Khodaskovskiy [12].

3. Experimental Methods

3.1. Batch Method

The purpose of the solubility measurements below 50°C using the batch method was to determine the time required to establish equilibrium between the solid phase and solution. The time to establish equilibrium, in turn, determined experimental parameters such as flow rate and the quantity of solid sample required for the flow through apparatus. These results were also used to verify the results obtained in the high-temperature flow-through solubility apparatus.

The batch-method measurements were carried out using a circulated water thermostat. The experiments were carried out in Nalgene bottles (high-density polyethylene, HDPE) using high-purity ("Millipore") water.

To avoid the uptake of carbon dioxide in the test solutions, ultra-high-purity (UHP) argon was used to purge the Nalgene bottle and water for 30 min before addition of the lead compound. The solutions were then sealed without contacting air for the equilibration period. A magnetic stirrer bar was used to stir the solutions slowly for 24 h. Stirring was then stopped and the solution was sampled after sitting for an additional 12 h to avoid sampling particulates suspended in the solution during sampling and to ensure that equilibrium is reached.

Ten millilitres of solution were filtered through a 0.2 μm pore size syringe filter to remove particulates. The solution was then sampled with an additional two or three times at 24 h intervals. The samples were stored in sealed polyethylene vials for measuring pH and electrical conductivity, and acidified for ICP-MS analysis to determine the total Pb concentration. The concentration of dissolved lead species at different times was used to determine the equilibration time of the dissolution reactions and the solubility of the lead compounds.

3.2. High-Temperature Solubility Test Apparatus

The measurement of lead solubility from 50 to 300°C was conducted at 9.65 MPa (absolute) using a high temperature flow-through system made from titanium. The schematic diagram of the facility and the flow direction of solution in the autoclave are shown in Figure 3. The major advantages of flow-through methods for solubility measurements have been summarized by Wesolowski et al. [13].

The autoclave was manufactured by Autoclave Engineers Inc., and has a design pressure of 13.79 MPa and a design temperature of 316°C. It consists of two titanium reaction vessels. The inner autoclave or sample holder is used to hold the lead compounds and has an internal diameter of 25.4 mm (1 in.) and volume of 50 mL. To prevent particulates from entering the flowing systems, two titanium filters with pore sizes of 30 µm are installed to sandwich the sample powder, and a silver membrane with a 0.2 µm pore size is installed at the outlet of the autoclave, as shown in Figure 4. A titanium spacer and the lid of inner autoclave are used to fix the position of the powder sample. A helical tube surrounds the outside surface of the inner autoclave and is immersed in water in the large outer autoclave. The lid of the large autoclave has a thermal well used to hold a thermocouple for temperature measurements of the inner autoclave. The entire autoclave is placed in an oven, which is thermostatically controlled to within ±1°C.

A 10-L titanium feed tank is used to continuously deliver the solution for the dissolution reaction to the autoclave. The feed solution is purged by ultra-pure argon to remove carbon dioxide and prevent air ingress. Depending on the equilibration time for sample dissolution, the flow rate of the solution can be precisely controlled from 0.05 to 1.5 mL/min by a positive displacement pump. The pump has a maximum pressure of 34.5 MPa and its wetted parts are made of 316 stainless steel, sapphire and UHMW polyethylene. Thus, depending on the flow rate and amount of lead compound in the autoclave, the residence time for the dissolution reaction can range from about 10 min to a maximum of 8 h. Duplicate measurements were performed under selected conditions using two flow rates, to confirm that the selected contact time was sufficient.

The temperatures of the autoclave, oven and sampled solutions and the pressure of the pressure relieve valves of sampling lines are continuously recorded by a Keithley 2700 Data Acquisition System, Model 7700, with 20 channels.

About ten millilitres of solution was taken and stored in sealed polyethylene vials for measuring pH and electrical conductivity, and acidified for ICP-MS analysis to determine the total Pb concentration. The identity of the solid phase ($PbSO_4$) was confirmed after selected measurements using X-ray diffraction.

The sample coolers were checked for lack of accumulation of lead by occasional washing with diluted nitric acid.

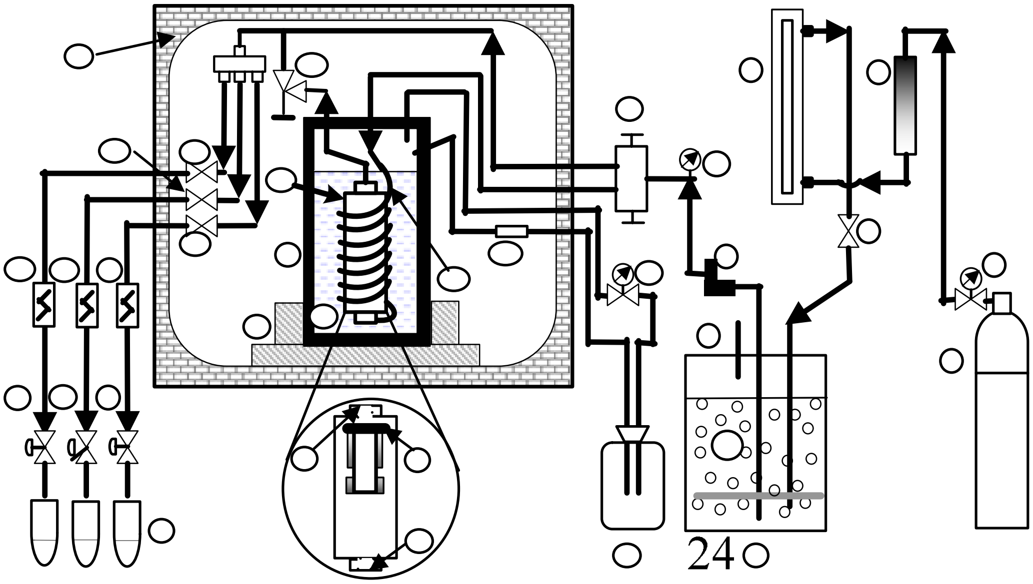

Figure 3 Schematic diagram of the flow through solubility apparatus

1) gas cylinder; **2)** control valve with pressure gauge; **3)** gas purifier; **4)** flow-meter; **5)** valve for purified gas; **6)** feed solution tank; **7)** container open to atmosphere; **8)** feed water under purge; **9)** vent line; **10)** feed pump; **11)** pressure indicator; **12)** control valve for feed flow; **13)** control valve with pressure indicator; **14)** rupture disk; **15)** helical tubing; **16)** water; **17)** inner autoclave; **18)** outer autoclave; **19)** control valve; **20-22)** outlet control valves; **23)** autoclave support; **24)** oven; **25-27)** heat exchangers for sample lines; **28-30)** back pressure relief valves for sample lines **31)** sample containers; **32)** outlet of inner autoclave; **33)** filter inside the inner autoclave; **34)** inlet of inner autoclave.

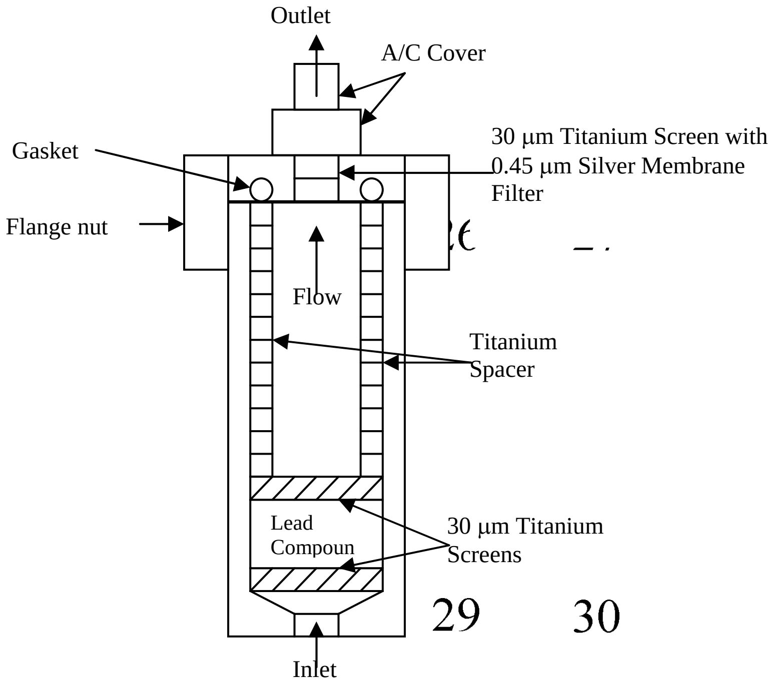

Figure 4 Schematic diagram of the inner titanium autoclave.

4. Experimental Results and Discussion

4.1 Solubility of $PbSO_4$ in Water

The solubility data of $PbSO_4$ (Figure 5) at 25°C and those above 25°C were determined using the batch method and flow-through method with flow rate ranging from 0.6 to 1.5 ml/min., respectively. These flow rates correspond to a residence time of 11 to 25 minutes. Kinetic experiment [9] showed that dissolution of $PbSO_4$ in pure water reached equilibrium within 1.5 hour at 25°C and 15 minutes at 60°C. The solubility data at different flow rates are consistent within the experimental uncertainty and agree very well with those of Clever and Johnson [7] and Kornicker et al. [9], indicating that the dissolution of $PbSO_4$ in batch method and flow through method reached equilibrium.

The pH values of the sampled solutions at 25°C generally range from 5.0 to 5.5. A buffer solution was not used to control the pH because of the possible formation of complexes with the buffer and safety issues. The concentrations of SO_4^{2-} in solution, and the effects of SO_4^{2-} and pH on the solubility of lead sulphate will be determined in the future experiments.

Preliminary solubility data obtained using the flow through method suggest that the solubility of $PbSO_4$ in water reaches a maximum around 50°C; above 100°C, the solubility of $PbSO_4$ is almost independent of temperature within experimental uncertainty (Figure 5).

Hydrolysis and complexing of Pb^{2+} in aqueous solutions were neglected by Böttger [6]. Kolthoff et al. [14] measured the solubility of $PbSO_4$ in Na_2SO_4 at 25°C and did not find lead forming a complex ion with sulphate even at high sulphate concentration. However, Hachimi et al. [15] examined the literature data and concluded that the solubility of $PbSO_4$ is controlled by the reaction,

$$PbSO_4(s) = Pb^{2+} + SO_4^{2-} \qquad \text{(Eq. 1)}$$

and the formation of complexing species $PbSO_4(aq)$. All of these authors did not consider the hydrolysis of Pb^{2+} in aqueous solutions at 25°C.

Hydrolysis reaction of

$$SO_4^{2-} + H_2O = HSO_4^- + OH^- \qquad \text{(Eq. 2)}$$

is not important below 200°C using the dissociation equilibrium constant of HSO_4^- [16]. For example, only 0.03% and 5% of total sulphate are present as HSO_4^- at 25 and 175°C, respectively, in the $PbSO_4$ dissolved solution.

Using critically reviewed literature data [8] of the hydrolysis reaction,

$$Pb^{2+} + H_2O = Pb(OH)^+ + H^+ \qquad \text{(Eq. 3)}$$

and the complexing reaction,

$$Pb^{2+} + SO_4^{2-} = PbSO_4\ (aq) \qquad \text{(Eq. 4)}$$

the authors of the paper calculated the concentrations of the hydrolysed species $PbOH^+$ and the complexing species $PbSO_4$ (aq) in the $PbSO_4$ dissolved solution at 25°C. It was found that the concentrations of $Pb(OH)^+$ and $PbSO_4$ (aq) are about 0.4% and 7% of the total dissolved lead, respectively. The concentration of $Pb(OH)^+$ was estimated to be 2% of total dissolved Pb using our measured pH at 25°C. Given the experimental uncertainty of solubility measurement, it is reasonable to ignore the hydrolysis of Pb^{2+} and the formation of other complexes such as $PbSO_4$(aq) at 25°C.

The solubility product constant, K_{sp}, of $PbSO_4$ can be calculated from its solubility in water,

$$K_{sp} = a_{Pb^{2+}} a_{SO_4^{2-}} \qquad \text{(Eq. 5)}$$

where $a_{Pb^{2+}}$ and $a_{SO_4^{2-}}$ are the activities of Pb^{2+} and SO_4^{2-}, respectively.

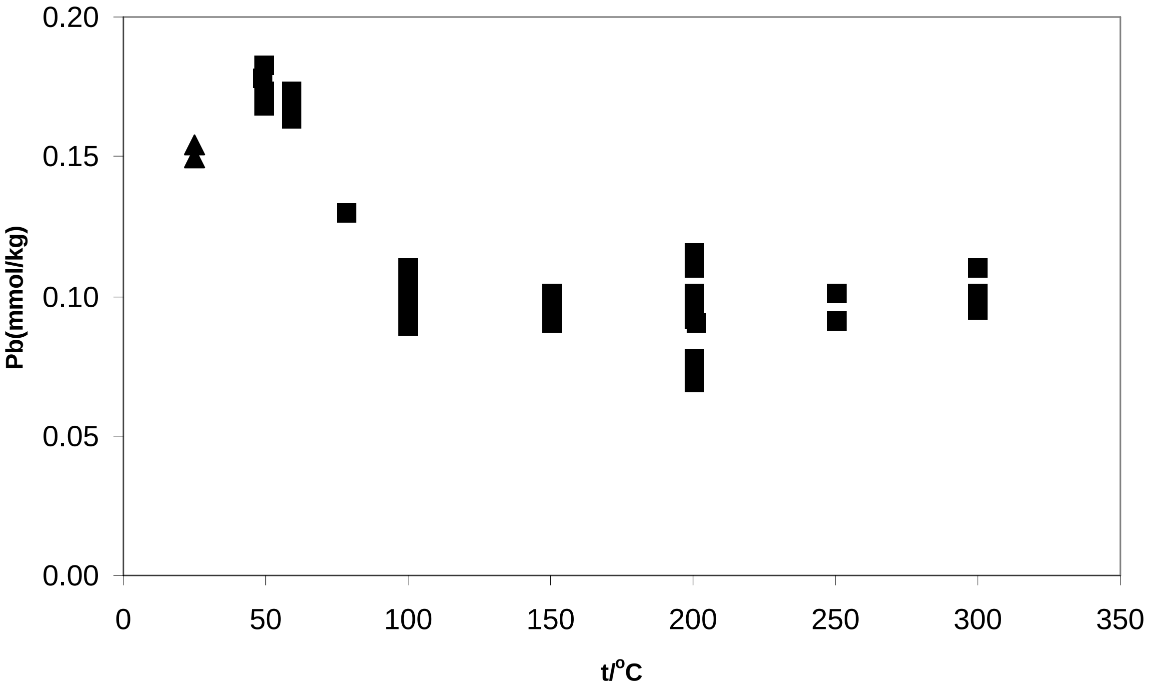

Figure 5 Preliminary data on the solubility of $PbSO_4$ in water from 25 to 300°C determined using the flow through method. The data at 25°C (▲) were determined using the batch method.

Assuming no ion pair formation such as $PbSO_4$(aq) and no Pb hydrolysis in solution, the mean activity coefficients, $\gamma_\pm$ of $PbSO_4$ were estimated using the extended Debye-Hückel equation,

$$\log \gamma_\pm = -AZ_+Z_- \frac{\sqrt{I}}{1+B\sqrt{I}} \qquad \text{(Eq. 6)}$$

where *A* and *B* are constants [17]; *I* is the ionic strength; and Z_+ and Z_- are the charges of cation and anion. The measured total Pb concentrations was used as the concentration of Pb^{2+} and SO_4^{2-}. The solubility product, 1.85×10^{-8}, at 25°C estimated from our experimental data, 0.152 mmol/kg, lies between the values of 1.62×10^{-8} recommended by Smith and Martell [8] and 2.53×10^{-8} by Clever and Johnson [7].

It is noted that neglecting hydrolysis and complexes probably is not valid at high temperatures. This issue will be addressed when the data on solubility of $PbSO_4$ as a function of pH become available and the K_{sp} above 25°C will be reported.

4.2. Solubility of $PbSO_4$ in NaCl solutions

To assess the effect of ionic strength on the concentration of dissolved lead species the solubility of $PbSO_4$ was measured by the batch method at 30, 50 and 70°C in various NaCl solutions (Figure 6). The solubility of $PbSO_4$ increases with increasing concentration of NaCl and increasing temperature.

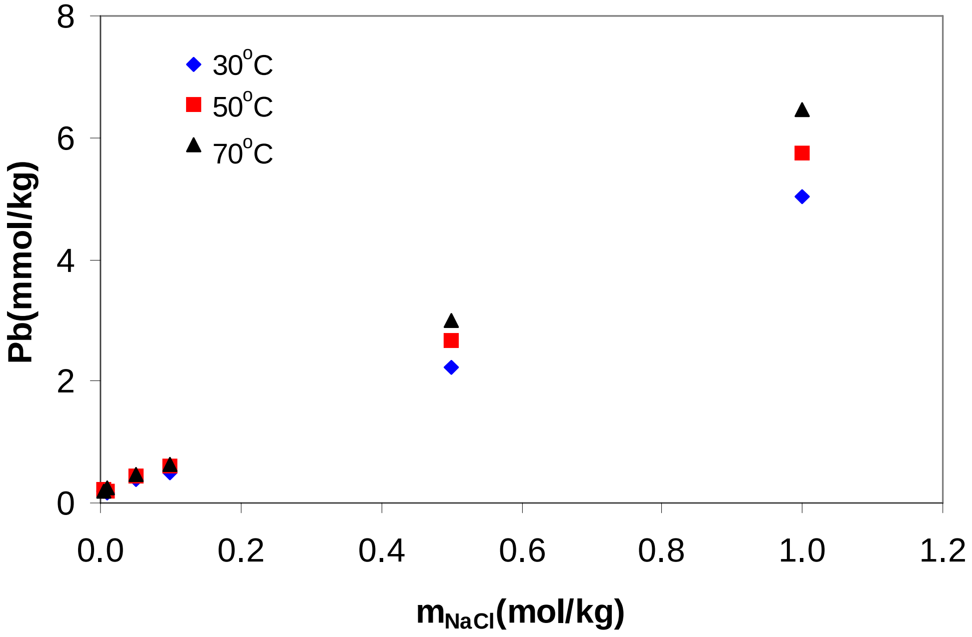

Figure 6 Solubility of $PbSO_4$ as a function of NaCl concentration and temperature.

Unlike the solubility in pure water where a maximum was observed at 50°C, the solubility of $PbSO_4$ in the presence of NaCl increases with increasing temperature from 30 to 70°C.

The variation in the measured solubility of $PbSO_4$ as a function of the concentration of NaCl is consistent with that predicted using electrolyte solution theory. For a sparingly soluble salt, the relation between solubility and activity coefficient can be expressed as [18]:

$$\ln S(c) = \ln S(0) - \ln \gamma_{\pm} \qquad \text{(Eq. 7)}$$

where $S(c)$ and $S(0\ )$ are the solubilities of the sparingly soluble salt in electrolyte solution and pure water, respectively; and $\gamma_{\pm}$ is the mean activity coefficient of the salt in solution.

If the mean activity coefficient is represented by the Pitzer equation [19], equation (2) becomes

$$\ln S(c) = \ln S(0) + Z_{+} Z_{-} A_{\varphi} \left[\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b} \ln(1 + b\sqrt{I}) \right] \qquad \text{(Eq. 8)}$$

where Z_+ and Z_- are the charges of the cation and anion in the sparingly soluble salt, respectively; A_φ is the Debye-Hückel osmotic parameter [17]; and b has a value of 1.2. Therefore, a plot of ln $S(c)$ vs.

$$\frac{\sqrt{I}}{1+b\sqrt{I}}+\frac{2}{b}\ln(1+b\sqrt{I}) \qquad \text{(Eq. 9)}$$

should be linear. The solubility data for $PbSO_4$ in NaCl are plotted in this manner in Figure 7 and the expected linear behaviour is observed over the range of ionic strengths studied.

This shows that the effect of ionic strength effect on $PbSO_4$ can be represented well by the Pitzer equation.

5. Conclusions

Preliminary data on the solubility of $PbSO_4$ was determined in pure water from 25 to 300°C using a combination of batch method and flow-through method, from which the solubility product constant at 25°C was calculated. These results show that $PbSO_4$ has a maximum solubility at 50°C, and above 100°C the solubility is almost independent of temperature within experimental error. Because of the possibility of ion pairs and hydrolysis at high temperatures, additional data are required before the solubility products at high temperature can be calculated.

The solubility of $PbSO_4$ increases with increasing NaCl concentration and temperature and the behaviour can be described by the Pitzer equation. Measurements of the solubility of $PbSO_4$ in NaCl solutions indicate that impurities present in SGs can increase the concentration of dissolved lead species through the effect of ionic strength.

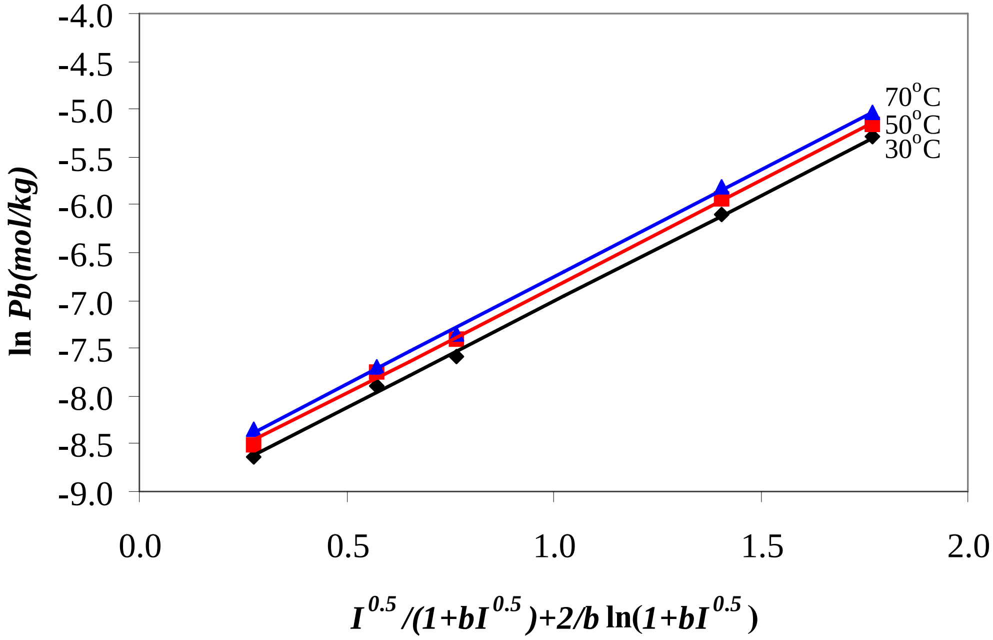

Figure 7 Solubility of $PbSO_4$ in NaCl solutions at temperature 30 (◆), 50 (■), and 70°C (▲), respectively.

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7. References

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