

1 A Pitzer Model for Lead Oxide Solubilities in the Presence  
2 of Borate to High Ionic Strength

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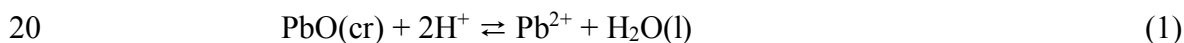
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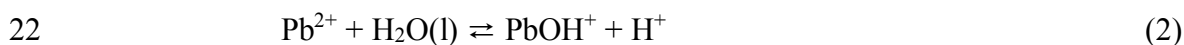
11 ABSTRACT

12 In this study, the hydrolysis model for lead applicable to high ionic strength is  
13 developed based on lead oxide solubilities as a function of ionic strength. Solubility  
14 measurements on lead oxide,  $\alpha$ -PbO (tetragonal, red, mineral name litharge), as a  
15 function of ionic strength are conducted in NaClO<sub>4</sub> solutions up to  $I = 0.45 \text{ mol}\cdot\text{kg}^{-1}$ , in  
16 NaCl solutions up to  $I = 5.0 \text{ mol}\cdot\text{kg}^{-1}$ , and in Na<sub>2</sub>SO<sub>4</sub> solutions up to  $I = 5.4 \text{ mol}\cdot\text{kg}^{-1}$ , at  
17 room temperature ( $22.5 \pm 0.5^\circ\text{C}$ ). The lead hydroxyl species considered in this work  
18 include the following,

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29 The equilibrium constants for Reactions (1) and (2) were taken from literature.

30 The equilibrium constants for Reactions (3) and (4) are determined in this study as -17.05

31 and -27.99, respectively, with a set of Pitzer parameters describing the interactions with

32 Na<sup>+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>.

33 In combination with the parameters from literature including those that have

34 already been published by our group, the solution chemistry of lead in a number of media

35 including NaCl, MgCl<sub>2</sub>, NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaClO<sub>4</sub>, and their mixtures, can be  
36 accurately described in a wide range of ionic strengths.

37

38 1. INTRODUCTION

39 An accurate understanding of solution chemistry/geochemistry of lead over a  
40 wide range of ionic strengths is important to many fields. For instance, in the field of  
41 mineral deposits, non-sulfide lead and zinc deposits are formed by the supergene  
42 alteration of various types of sulfidic lead and zinc deposits. In the supergene alteration  
43 processes, solutions with multiple components including sulfate and chloride having a  
44 range of ionic strengths are responsible for transport and deposition of lead and zinc  
45 (Potter and Nordstrom, 1978; Mann and Deutscher, 1980; Doepker and Drake, 1991;  
46 Awoh et al., 2014). Thus, accurate knowledge of interactions of lead with multiple  
47 components in solutions is a prerequisite for modeling the supergene alteration processes  
48 of sulfidic lead and zinc deposits, and formation of non-sulfide lead and zinc deposits.

49 In the field of nuclear waste management, there are significant inventories of lead  
50 in nuclear waste stream destined for disposal in the geological repositories. For instance,  
51 there are sizable inventories of lead in both the waste stream and in shielding materials in  
52 the Waste Isolation Pilot Plant (WIPP) (U.S. EPA, 2015; Xiong et al., 2015). It was  
53 estimated that the total inventory for lead, including lead in contact handled (CH) and  
54 remote handled (RH) waste as well as packaging, in the WIPP was on the order of  
55 1,256,796 kg (Xiong et al., 2015). That lead is likely to interact with brines that are part  
56 of the salt formation where WIPP is located. Two brines in particular, Generic Weep  
57 Brine (GWB) from the Salado Formation, and Energy Research and Development  
58 Administration (WIPP Well) 6 (ERDA-6) from the Castile Formation, have ionic  
59 strengths up to  $8.26 \text{ mol} \cdot \text{kg}^{-1}$  (Xiong and Lord, 2008). Further, cerussite ( $\text{PbCO}_3$ ) has

60 been proposed as a waste form for geological disposal of radioactive  $^{14}\text{C}$  generated in the  
61 heavy-water moderator systems of nuclear reactors (Taylor and Lopata, 1984).

62         Additionally, in the Argentina repository design, the containers for reprocessed  
63 and vitrified wastes have a thick intermediate layer that is made of lead with a 10 cm  
64 width (Cassibba and Fernandez, 1989; Semino et al., 1993, 1996; Guasp et al., 2000),  
65 owing to its excellent radiological protection and corrosion resistance. In Russia, lead  
66 and lead-based alloys are also considered as prospective matrices as containers for used  
67 nuclear fuel, lead and lead-based alloys are being used for conditioning spent sealed  
68 radioactive sources at radioactive waste disposal facilities (Arustamov et al., 1999;  
69 Ojovan et al., 1999, 2003, 2004). Lead containers are also used in the Brazil repository  
70 design (Vicente, 2007a, 2007b).

71         Clearly, the chemistry of lead will impact the near-field geochemical conditions in  
72 geological repositories. In our previous publications, we have addressed the solution  
73 chemistry of lead in the presence of oxalate (Xiong et al., 2013), and in carbonate-  
74 containing systems (Xiong, 2015), in a wide range of ionic strengths.

75         In this work, we investigate the interactions of lead hydroxyl species with the  
76 desired media in mildly alkaline pH range via solubility measurements on lead oxide,  
77 litharge. The primary reason for choosing litharge as a solubility-controlling phase for  
78 solubility measurements is that litharge could be a solubility-controlling phase under  
79 alkaline conditions in natural low temperature environments (Xiong et al., 2013).

80         There are two natural crystalline phases for lead monoxide, i.e., litharge and  
81 massicot (Pencival, 1925). Litharge is red, which is denoted as  $\alpha\text{-PbO}$  with a tetragonal  
82 crystal structure, whereas massicot is yellow, denoted as  $\beta\text{-PbO}$  with an orthorhombic

83 crystal structure (Ziemniak et al., 2005). Litharge is the thermodynamically more stable  
84 oxide than massicot and hydrous lead(II) oxide (Ziemniak et al., 2005).

85 An added advantage for performing solubility measurements on litharge is that  
86 litharge frequently occurs in various environments. For example, after lead pipe was  
87 buried in various soils for ten years, litharge was of the corrosion products (Gilbert,  
88 1947). The tested soils included wet acid peat (pH 4.3), moist acid clay (pH 4.6), dry  
89 acid sand (pH 5.1), slightly acid sand (pH 6.0), moist normal clay (pH 7.1), chalk (pH  
90 8.2–8.4) (Gilbert, 1947). When archaeological lead artifacts were corroded in soils with  
91  $\text{pH} > 6.5$ , the corrosion products were 70% as litharge and 20% as cerussite ( $\text{PbCO}_3$ ) in  
92 volume (Reich et al., 2003). Tylecote (1983) concluded that litharge was a major  
93 corrosion product for land-based lead from archaeological sources. Litharge can also  
94 form when nickel-based alloys are subject to stress corrosion owing to trace level  
95 concentrations of lead in nuclear reactor coolants under hydrothermal conditions in high  
96 temperature environments (Ziemniak et al., 2005).

97 Based on solubility data, we develop a Pitzer model to describing solubilities of  
98 litharge over a wide range of ionic strengths. As mentioned above, litharge is often  
99 observed in various environments. Therefore, the Pitzer model developed in this study  
100 can be applied to modelling solubilities of litharge under various conditions pertaining its  
101 stability.

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104 2. EXPERIMENTAL SECTION

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106 In these solubility experiments, about 2 grams of litharge—ACS reagent grade  
107 lead oxide (CAS 1317-36-8) from MP Biomedicals was weighed out and placed into 150  
108 mL plastic bottles. Then, 100 mL of supporting electrolyte solution were added to those  
109 bottles. Once filled, the lids of the bottles were sealed with parafilm.

110 The supporting electrolytes are a series of NaCl solutions ranging from 0.010  
111 mol•kg<sup>-1</sup> to 5.0 mol•kg<sup>-1</sup>, Na<sub>2</sub>SO<sub>4</sub> solutions ranging from 0.010 mol•kg<sup>-1</sup> to 1.8 mol•kg<sup>-1</sup>,  
112 and NaClO<sub>4</sub> solutions ranging from 0.1 mol•kg<sup>-1</sup> to 0.45 mol•kg<sup>-1</sup>. The supporting  
113 electrolyte solutions were prepared from degassed deionized (DI) water. The degassed  
114 DI water was prepared by following a procedure similar to that used by Wood et al.  
115 (2002) to remove dissolved CO<sub>2</sub>. The undersaturation experiments are conducted at  
116 laboratory room temperature (22.5 ± 0.5°C).

117 The pH readings were measured with an Orion-Ross combination pH glass  
118 electrode, coupled with an Orion Research EA 940 pH meter that was calibrated with  
119 three pH buffers (pH 4, pH 7, and pH 10). In solutions with an ionic strength higher than  
120 0.10 mol•kg<sup>-1</sup>, hydrogen-ion concentrations on molar scale (pcH) were determined from  
121 pH readings by using correction factors for NaCl and Na<sub>2</sub>SO<sub>4</sub> solutions determined by  
122 Rai et al. (1995). The correction factors for NaClO<sub>4</sub> were approximated by using those  
123 of NaCl. Based on the equation in Xiong et al. (2010), pcHs are converted to hydrogen-  
124 ion concentrations on the molal scale (pmH).

125 Solution samples were periodically withdrawn from experimental runs. Before  
126 solution samples were taken, pH readings of experimental runs were measured. The  
127 sample size was usually 3 mL. After a solution sample was withdrawn from an  
128 experiment and filtered with a 0.2 µm syringe filter, the filtered solution was then

129 weighed, acidified with 0.5 mL of concentrated TraceMetal<sup>®</sup> grade HNO<sub>3</sub> from Fisher  
130 Scientific, and finally diluted to a volume of 10 mL with DI water. If subsequent  
131 dilutions were needed, aliquots were taken from the first dilution samples for the second  
132 dilution, and aliquots of the second dilution were then taken for further dilution.

133           Lead concentrations of solutions were analyzed with a Perkin Elmer dual-view  
134 inductively coupled plasma-atomic emission spectrometer (ICP-AES)  
135 (Perkin Elmer DV 3300). Calibration blanks and standards were precisely matched with  
136 experimental matrices. The linear correlation coefficients of calibration curves in all  
137 measurements were better than 0.9995. The analytical precision for ICP-AES is better  
138 than 1.00% in terms of the relative standard deviation (RSD) based on replicate analyses.

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## 142 3. EXPERIMENTAL RESULTS, AND THERMODYNAMIC MODELING

### 143 3.1 Experimental Results

144 Experimental results for solubilities of litharge in NaClO<sub>4</sub>, NaCl and Na<sub>2</sub>SO<sub>4</sub>  
145 solutions are tabulated in Tables 1, 2 and 3, and displayed in Figures 1 through 3,  
146 respectively.

147 In Figure 1, the experimental results in NaClO<sub>4</sub> solutions are presented. The  
148 results in 0.30, 0.40 and 0.45 mol•kg<sup>-1</sup> indicate that the steady state concentrations within  
149 experimental uncertainties were reached, starting from the second sampling (i.e., 272  
150 days, see Table 1). However, there are slightly larger scatters for the results in lower  
151 ionic strengths, especially in 0.1 mol•kg<sup>-1</sup> (Figure 1).

152 The experimental results for experiments in NaCl solutions are displayed in  
153 Figure 2. The results demonstrate that the steady state concentrations within  
154 experimental uncertainties are reached in the first sampling, i.e., 155 days (see Table 2).

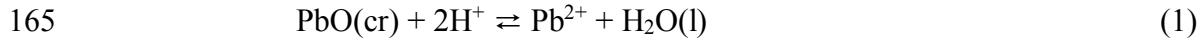
155 The results for experiments in Na<sub>2</sub>SO<sub>4</sub> solutions are plotted in Figure 3. Similarly  
156 to the results in NaCl, the results in Na<sub>2</sub>SO<sub>4</sub> solutions suggest that the steady state  
157 concentrations within experimental uncertainties are reached in the first sampling  
158 (Figure 3), i.e., 162 days (see Table 3).

159

### 160 3.2 Thermodynamic Modeling

161 In the following, the experimental data described above are used to derive the  
162 thermodynamic parameters. The dissolution of litharge, α-PbO(cr), in NaClO<sub>4</sub> solutions  
163 can be expressed as,

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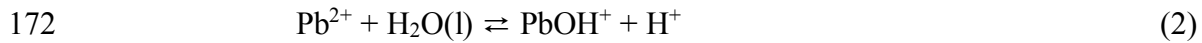


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167 Since  $\text{ClO}_4^-$  from  $\text{NaClO}_4$  solutions is not a complexing agent with  $\text{Pb}^{2+}$ , the Pb-  
168 containing species contributing to total lead concentrations are  $\text{Pb}^{2+}$ ,  $\text{PbOH}^+$ ,  
169  $\text{Pb}(\text{OH})_2(\text{aq})$ , and  $\text{Pb}(\text{OH})_3^-$ , in equilibrium with  $\text{PbO}(\text{cr})$  in  $\text{NaClO}_4$  solutions.

170 Formation of lead hydroxyl complexes can be cast as follows:

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175

176 In the modeling, the equilibrium constants for Reaction (1), and Reactions (2) are  
177 taken from Wolery and Jarek (2003), and Powell et al. (2009), respectively. In the first  
178 step of modeling, the equilibrium constants for Reactions (3) and (4) are obtained by  
179 matching experimental data. The strategy for modeling these two equilibrium constants  
180 is to use the solubility data in lower ionic strength where the interactions between the  
181 lead hydroxyl complexes and the media are weak and negligible. To achieve this  
182 objective, the experimental data at  $0.1 \text{ mol}\cdot\text{kg}^{-1}$  in  $\text{NaClO}_4$  and at  $0.01 \text{ mol}\cdot\text{kg}^{-1}$  and  $0.1$   
183  $\text{mol}\cdot\text{kg}^{-1}$  in  $\text{NaCl}$  solutions are selected.

184 The computer code, EQ3/6 Version 8.0a (Wolery et al., 2010; Xiong, 2011), is  
185 used as the modeling platform, which was also used in previous modeling work for  
186 obtaining thermodynamic properties including the Pitzer parameters (e.g., Xiong et al.,  
187 2013, 2017; Xiong, 2013, 2015). The database containing all parameters necessary

188 including thermodynamic properties for the modeling, is data0.fm1 (Xiong, 2011). In the  
189 database, data0.fm1, the interaction parameters for major ions are from Harvie et al.  
190 (1984), and the interaction parameters for organic ligands are from Choppin et al. (2001).

191 In the model fitting, the experimental data were first used to generate EQ3/6 input  
192 files. Then, a script such as a Python script was generated to call the targeted parameters,  
193 and call EQ3/6. The minimization subroutine in the script automatically compares total  
194 sum of squared residuals between experimental values [i.e., total lead concentrations,  
195  $\Sigma\text{Pb(II)}/\text{mol}\cdot\text{kg}^{-1}$ ] and model-predicted values produced by a set of inputted parameters  
196 in each iteration. The iteration is completed when the total sum of squared residuals  
197 reaches a minimum.

198 The hydrolysis constants for Reactions (3) and (4) obtained in our modeling with  
199 our solubility data are  $-17.05$  and  $-27.99$  (Table 4). These values are in excellent  
200 agreement with the respective values of  $-16.94$  and  $-28.03$  for these two reactions  
201 recommended by Powell et al. (2009) using the Specific Ion Interaction Theory (SIT)  
202 model for extrapolation to infinite dilution. The excellent agreement indicates that our  
203 solubility data agree well with the previous experimental data obtained with various  
204 methods including potentiometric titration and solubility studies that were accepted in the  
205 review by Powell et al. (2009).

206 With these hydrolysis constants, the interactions of  $\text{Pb(OH)}_2(\text{aq})$  and  $\text{Pb(OH)}_3^-$   
207 with media are modeled (Table 4).

208 In Table 4, the dissolution constant for litharge, the formation constants for lead  
209 hydroxyl species, and a set of Pitzer parameters describing the specific interactions of  
210 citrate species in  $\text{NaClO}_4$ ,  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  media are listed. These Pitzer parameters

211 are similar to those found in the literature for the similar interactions in terms of  
212 magnitude. For instance, the  $\beta^{(0)}$  for  $\text{Na}^+—\text{Pb}(\text{OH})_3^-$  interaction, a 1:1 interaction, is  
213 0.3354 (Table 4), which is similar to the  $\beta^{(0)}$  of 0.43 for  $\text{Na}^+—\text{H}_3\text{SiO}_4^-$  interaction  
214 (Hershey and Millero, 1986), also a 1:1 interaction.

215 It should be noted that the  $\beta^{(1)}$ 's in Table 3 were not calculated. Instead, they are  
216 pre-set to the average values for the respective interactions, following the paradigm of  
217 Choppin et al. (2001). In Choppin et al. (2001), they calculated and recommended a set  
218 of average values of  $\beta^{(1)}$ 's for various interactions (e.g., 1:1, 1:2/2:1, 1:3/3:1, etc.,  
219 interactions), based on the  $\beta^{(1)}$  values for respective interactions from literature.

220 In Figures 4 through 8, solubilities predicted by using the model developed in this  
221 study are compared with the experimental values in  $\text{NaClO}_4$ ,  $\text{NaCl}$ , and  $\text{Na}_2\text{SO}_4$  solutions  
222 produced in this work. It is clear from these figures that the model reproduces the  
223 experimental data well. In addition, the experimental data in  $\text{NaOH}$  (Garrett et al., 1939)  
224 and  $\text{KOH}$  (Randall and Spencer, 1928), independent from the model, are also compared  
225 with the model-predicted values. These figures demonstrate that the model-predicted  
226 values are in good agreement with those model-independent experimental data, validating  
227 our model.

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229

#### 230 4. CONCLUSIONS

231 Long-term solubility measurements up to 1,461 days and to high ionic strengths  
232 for litharge in  $\text{NaClO}_4$ ,  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  solutions produced at Sandia National  
233 Laboratories Carlsbad Facility are presented in this work. A Pitzer model is developed

234 based on these solubility measurements. This model would provide accurate descriptions  
235 about the interactions of lead with  $\text{NaClO}_4$ ,  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  matrixes under various  
236 conditions with applications to many fields such as nuclear waste management and  
237 modeling the formation of non-sulfide lead deposits during the supergene alteration  
238 processes.

239

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Table 1. Experimental results concerning solubility of litharge,  $\alpha$ -PbO(cr), in NaClO<sub>4</sub> solutions produced at SNL at  $22.5 \pm 0.5$  °C.

Experimental Number	Supporting Medium, NaClO <sub>4</sub> , molal	Experimental time, days	pmH*	Solubility expressed as total lead on molal scale, $m_{\Sigma Pb}$
PbB4O7-0.1ClO4-1	0.10	223	10.68	4.58E-05
PbB4O7-0.1ClO4-1	0.10	223	10.65	3.86E-05
PbB4O7-0.2ClO4-1	0.20	223	10.83	8.69E-05
PbB4O7-0.2ClO4-1	0.20	223	10.86	9.97E-05
PbB4O7-0.3ClO4-1	0.30	223	10.89	1.27E-04
PbB4O7-0.3ClO4-1	0.30	223	10.85	1.42E-04
PbB4O7-0.4ClO4-1	0.40	223	11.12	1.67E-04
PbB4O7-0.4ClO4-1	0.40	223	11.15	1.77E-04
PbB4O7-0.45ClO4-1	0.45	223	11.17	1.93E-04
PbB4O7-0.45ClO4-1	0.45	223	11.03	1.92E-04
PbB4O7-0.1ClO4-1	0.10	272	10.67	7.38E-05
PbB4O7-0.1ClO4-1	0.10	272	10.64	7.58E-05
PbB4O7-0.2ClO4-1	0.20	272	10.83	1.23E-04
PbB4O7-0.2ClO4-1	0.20	272	10.84	1.22E-04
PbB4O7-0.3ClO4-1	0.30	272	10.93	1.58E-04
PbB4O7-0.3ClO4-1	0.30	272	10.95	1.60E-04
PbB4O7-0.4ClO4-1	0.40	272	11.04	1.93E-04
PbB4O7-0.4ClO4-1	0.40	272	11.03	2.03E-04
PbB4O7-0.45ClO4-1	0.45	272	11.11	2.25E-04
PbB4O7-0.45ClO4-1	0.45	272	11.12	2.05E-04
PbB4O7-0.1ClO4-1	0.10	318	10.74	5.86E-05
PbB4O7-0.1ClO4-1	0.10	318	10.68	4.61E-05
PbB4O7-0.2ClO4-1	0.20	318	10.87	9.22E-05
PbB4O7-0.2ClO4-1	0.20	318	10.88	1.00E-04
PbB4O7-0.3ClO4-1	0.30	318	10.96	1.38E-04
PbB4O7-0.3ClO4-1	0.30	318	10.97	1.38E-04
PbB4O7-0.4ClO4-1	0.40	318	11.07	1.84E-04
PbB4O7-0.4ClO4-1	0.40	318	11.06	1.96E-04
PbB4O7-0.45ClO4-1	0.45	318	11.00	2.08E-04
PbB4O7-0.45ClO4-1	0.45	318	10.98	2.17E-04
PbB4O7-0.1ClO4-1	0.10	370	10.70	8.25E-05

PbB4O7-0.1ClO4-1	0.10	370	10.64	6.21E-05
PbB4O7-0.2ClO4-1	0.20	370	10.83	1.20E-04
PbB4O7-0.2ClO4-1	0.20	370	10.87	1.28E-04
PbB4O7-0.3ClO4-1	0.30	370	10.95	1.58E-04
PbB4O7-0.3ClO4-1	0.30	370	10.92	1.70E-04
PbB4O7-0.4ClO4-1	0.40	370	11.02	2.09E-04
PbB4O7-0.4ClO4-1	0.40	370	10.98	2.10E-04
PbB4O7-0.45ClO4-1	0.45	370	11.01	2.19E-04
PbB4O7-0.45ClO4-1	0.45	370	10.97	2.35E-04
PbB4O7-0.1ClO4-1	0.10	421	10.74	6.69E-05
PbB4O7-0.1ClO4-1	0.10	421	10.70	5.81E-05
PbB4O7-0.2ClO4-1	0.20	421	10.90	1.04E-04
PbB4O7-0.2ClO4-1	0.20	421	10.91	1.14E-04
PbB4O7-0.3ClO4-1	0.30	421	10.98	1.54E-04
PbB4O7-0.3ClO4-1	0.30	421	10.98	1.68E-04
PbB4O7-0.4ClO4-1	0.40	421	11.09	2.10E-04
PbB4O7-0.4ClO4-1	0.40	421	11.06	2.09E-04
PbB4O7-0.45ClO4-1	0.45	421	11.10	2.36E-04
PbB4O7-0.45ClO4-1	0.45	421	11.11	2.38E-04
PbB4O7-0.1ClO4-1	0.10	581	10.77	6.15E-05
PbB4O7-0.1ClO4-1	0.10	581	10.74	5.34E-05
PbB4O7-0.2ClO4-1	0.20	581	10.93	9.17E-05
PbB4O7-0.2ClO4-1	0.20	581	10.94	1.03E-04
PbB4O7-0.3ClO4-1	0.30	581	11.02	1.43E-04
PbB4O7-0.3ClO4-1	0.30	581	11.04	1.51E-04
PbB4O7-0.4ClO4-1	0.40	581	11.14	1.99E-04
PbB4O7-0.4ClO4-1	0.40	581	11.10	1.94E-04
PbB4O7-0.45ClO4-1	0.45	581	11.11	2.20E-04
PbB4O7-0.45ClO4-1	0.45	581	11.03	2.19E-04
PbB4O7-0.1ClO4-1	0.10	672	10.77	7.61E-05
PbB4O7-0.1ClO4-1	0.10	672	10.69	6.61E-05
PbB4O7-0.2ClO4-1	0.20	672	10.88	1.01E-04
PbB4O7-0.2ClO4-1	0.20	672	10.89	1.25E-04
PbB4O7-0.3ClO4-1	0.30	672	10.99	1.59E-04
PbB4O7-0.3ClO4-1	0.30	672	10.96	1.64E-04
PbB4O7-0.4ClO4-1	0.40	672	11.05	1.90E-04
PbB4O7-0.4ClO4-1	0.40	672	11.05	1.96E-04

PbB4O7-0.45ClO4-1	0.45	672	11.07	2.17E-04
PbB4O7-0.45ClO4-1	0.45	672	11.10	2.19E-04
PbB4O7-0.1ClO4-1	0.10	714	10.80	9.82E-05
PbB4O7-0.1ClO4-1	0.10	714	10.70	7.91E-05
PbB4O7-0.2ClO4-1	0.20	714	10.90	1.25E-04
PbB4O7-0.2ClO4-1	0.20	714	10.91	1.34E-04
PbB4O7-0.3ClO4-1	0.30	714	11.00	1.79E-04
PbB4O7-0.3ClO4-1	0.30	714	11.01	1.84E-04
PbB4O7-0.4ClO4-1	0.40	714	11.08	2.15E-04
PbB4O7-0.4ClO4-1	0.40	714	11.06	2.15E-04
PbB4O7-0.45ClO4-1	0.45	714	11.08	2.30E-04
PbB4O7-0.45ClO4-1	0.45	714	11.04	2.45E-04

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424 \* Values of pmH reported are calculated by using the correction factors ( $A_M$ ) from Rai et  
425 al. (1995) for pH readings, and conversion factors ( $\Theta$ ) from molarity to molality,  $\text{pmH} =$   
426  $\text{pH}_{\text{ob}} + A_M - \log \Theta$  (Xiong et al., 2010). The conversion factors are calculated from  
427 densities for NaClO<sub>4</sub> solutions, which are from Söhnel and Novotný (1985).  
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Table 2. Experimental results concerning solubility of litharge,  $\alpha$ -PbO(cr), in NaCl solutions in the presence of  $0.001 \text{ mol}\cdot\text{kg}^{-1} \text{ H}_3\text{BO}_3$  produced at SNL at  $22.5 \pm 0.5 \text{ }^\circ\text{C}$ .

Experimental Number	Supporting Medium, NaCl, $\text{mol}\cdot\text{kg}^{-1}$	Experimental time, days	pmH*	Solubility expressed as total lead on molal scale, $m_{\Sigma\text{Pb}}$
PbB(OH)4-0.01Cl-1	0.010	155	11.58	4.67E-04
PbB(OH)4-0.01Cl-2	0.010	155	11.59	5.03E-04
PbB(OH)4-0.1Cl-1	0.10	155	11.87	5.83E-04
PbB(OH)4-0.1Cl-2	0.10	155	11.89	6.57E-04
PbB(OH)4-1.0Cl-1	1.0	155	11.86	3.03E-04
PbB(OH)4-1.0Cl-2	1.0	155	11.99	2.98E-04
PbB(OH)4-2.0Cl-1	2.1	155	12.02	2.27E-04
PbB(OH)4-2.0Cl-2	2.1	155	11.93	1.83E-04
PbB(OH)4-3.0Cl-1	3.2	155	12.08	1.84E-04
PbB(OH)4-3.0Cl-2	3.2	155	12.09	1.90E-04
PbB(OH)4-4.0Cl-1	4.4	155	12.22	1.85E-04
PbB(OH)4-4.0Cl-2	4.4	155	12.24	1.71E-04
PbB(OH)4-5.0Cl-1	5.0	155	12.27	1.58E-04
PbB(OH)4-5.0Cl-2	5.0	155	12.27	1.51E-04
PbB(OH)4-0.01Cl-1	0.010	255	11.75	4.54E-04
PbB(OH)4-0.01Cl-2	0.010	255	11.75	4.87E-04
PbB(OH)4-0.1Cl-1	0.10	255	12.11	6.01E-04
PbB(OH)4-0.1Cl-2	0.10	255	12.12	5.67E-04
PbB(OH)4-1.0Cl-1	1.0	255	12.13	3.32E-04
PbB(OH)4-1.0Cl-2	1.0	255	12.12	3.14E-04
PbB(OH)4-2.0Cl-1	2.1	255	12.23	2.42E-04
PbB(OH)4-2.0Cl-2	2.1	255	12.18	2.03E-04
PbB(OH)4-3.0Cl-1	3.2	255	12.32	1.92E-04
PbB(OH)4-3.0Cl-2	3.2	255	12.32	2.04E-04
PbB(OH)4-4.0Cl-1	4.4	255	12.51	2.28E-04
PbB(OH)4-4.0Cl-2	4.4	255	12.49	1.88E-04
PbB(OH)4-5.0Cl-1	5.0	255	12.52	1.74E-04
PbB(OH)4-5.0Cl-2	5.0	255	12.52	1.56E-04
PbB(OH)4-0.01Cl-1	0.010	304	11.89	4.87E-04
PbB(OH)4-0.01Cl-2	0.010	304	11.88	5.32E-04
PbB(OH)4-0.1Cl-1	0.10	304	12.23	5.90E-04

PbB(OH)4-0.1Cl-2	0.10	304	12.23	5.58E-04
PbB(OH)4-1.0Cl-1	1.0	304	12.22	3.32E-04
PbB(OH)4-1.0Cl-2	1.0	304	12.22	3.33E-04
PbB(OH)4-2.0Cl-1	2.1	304	12.32	2.41E-04
PbB(OH)4-2.0Cl-2	2.1	304	12.29	2.30E-04
PbB(OH)4-3.0Cl-1	3.2	304	12.43	2.22E-04
PbB(OH)4-3.0Cl-2	3.2	304	12.46	1.97E-04
PbB(OH)4-4.0Cl-1	4.4	304	12.61	1.74E-04
PbB(OH)4-4.0Cl-2	4.4	304	12.57	1.78E-04
PbB(OH)4-5.0Cl-1	5.0	304	12.63	2.02E-04
PbB(OH)4-5.0Cl-2	5.0	304	12.71	2.25E-04
PbB(OH)4-0.01Cl-1	0.010	352	11.84	4.79E-04
PbB(OH)4-0.01Cl-2	0.010	352	11.81	5.27E-04
PbB(OH)4-0.1Cl-1	0.10	352	12.14	5.93E-04
PbB(OH)4-0.1Cl-2	0.10	352	12.13	5.78E-04
PbB(OH)4-1.0Cl-1	1.0	352	12.07	3.38E-04
PbB(OH)4-1.0Cl-2	1.0	352	12.05	3.19E-04
PbB(OH)4-2.0Cl-1	2.1	352	12.16	2.40E-04
PbB(OH)4-2.0Cl-2	2.1	352	12.06	2.07E-04
PbB(OH)4-3.0Cl-1	3.2	352	12.19	1.96E-04
PbB(OH)4-3.0Cl-2	3.2	352	12.16	2.28E-04
PbB(OH)4-4.0Cl-1	4.4	352	12.32	2.02E-04
PbB(OH)4-4.0Cl-2	4.4	352	12.33	1.98E-04
PbB(OH)4-5.0Cl-1	5.0	352	12.36	1.74E-04
PbB(OH)4-5.0Cl-2	5.0	352	12.35	1.51E-04
PbB(OH)4-0.01Cl-1	0.010	401	11.65	4.79E-04
PbB(OH)4-0.01Cl-2	0.010	401	11.48	5.25E-04
PbB(OH)4-0.1Cl-1	0.10	401	11.89	6.37E-04
PbB(OH)4-0.1Cl-2	0.10	401	11.90	6.16E-04
PbB(OH)4-1.0Cl-1	1.0	401	11.82	3.35E-04
PbB(OH)4-1.0Cl-2	1.0	401	11.83	3.17E-04
PbB(OH)4-2.0Cl-1	2.1	401	12.05	2.61E-04
PbB(OH)4-2.0Cl-2	2.1	401	11.99	2.12E-04
PbB(OH)4-3.0Cl-1	3.2	401	12.09	2.25E-04
PbB(OH)4-3.0Cl-2	3.2	401	12.28	2.32E-04
PbB(OH)4-4.0Cl-1	4.4	401	12.34	1.85E-04
PbB(OH)4-4.0Cl-2	4.4	401	12.32	1.94E-04
PbB(OH)4-5.0Cl-1	5.0	401	12.44	1.69E-04

PbB(OH)4-5.0Cl-2	5.0	401	12.37	1.60E-04
PbB(OH)4-0.01Cl-1	0.010	553	11.90	4.45E-04
PbB(OH)4-0.01Cl-2	0.010	553	11.90	4.80E-04
PbB(OH)4-0.1Cl-1	0.10	553	12.24	5.70E-04
PbB(OH)4-0.1Cl-2	0.10	553	12.20	5.67E-04
PbB(OH)4-1.0Cl-1	1.0	553	12.17	3.07E-04
PbB(OH)4-1.0Cl-2	1.0	553	12.16	3.07E-04
PbB(OH)4-2.0Cl-1	2.1	553	12.27	2.72E-04
PbB(OH)4-2.0Cl-2	2.1	553	12.21	2.19E-04
PbB(OH)4-3.0Cl-1	3.2	553	12.35	1.91E-04
PbB(OH)4-3.0Cl-2	3.2	553	12.33	1.90E-04
PbB(OH)4-4.0Cl-1	4.4	553	12.44	1.89E-04
PbB(OH)4-4.0Cl-2	4.4	553	12.43	1.77E-04
PbB(OH)4-5.0Cl-1	5.0	553	12.47	1.56E-04
PbB(OH)4-5.0Cl-2	5.0	553	12.44	1.42E-04
PbB(OH)4-0.01Cl-1	0.010	616	11.89	4.74E-04
PbB(OH)4-0.01Cl-2	0.010	616	11.89	5.08E-04
PbB(OH)4-0.1Cl-1	0.10	616	12.23	5.96E-04
PbB(OH)4-0.1Cl-2	0.10	616	12.20	6.01E-04
PbB(OH)4-1.0Cl-1	1.0	616	12.17	3.54E-04
PbB(OH)4-1.0Cl-2	1.0	616	12.17	3.27E-04
PbB(OH)4-2.0Cl-1	2.1	616	12.29	2.85E-04
PbB(OH)4-2.0Cl-2	2.1	616	12.22	2.27E-04
PbB(OH)4-3.0Cl-1	3.2	616	12.32	2.07E-04
PbB(OH)4-3.0Cl-2	3.2	616	12.40	2.04E-04
PbB(OH)4-4.0Cl-1	4.4	616	12.50	2.00E-04
PbB(OH)4-4.0Cl-2	4.4	616	12.51	1.83E-04
PbB(OH)4-5.0Cl-1	5.0	616	12.52	1.69E-04
PbB(OH)4-5.0Cl-2	5.0	616	12.47	1.58E-04
PbB(OH)4-0.01Cl-1	0.010	763	11.83	4.59E-04
PbB(OH)4-0.01Cl-2	0.010	763	11.81	4.80E-04
PbB(OH)4-0.1Cl-1	0.10	763	12.14	5.80E-04
PbB(OH)4-0.1Cl-2	0.10	763	12.14	5.88E-04
PbB(OH)4-1.0Cl-1	1.0	763	12.09	3.20E-04
PbB(OH)4-1.0Cl-2	1.0	763	12.05	3.06E-04
PbB(OH)4-2.0Cl-1	2.1	763	12.05	2.75E-04



PbB(OH)4-2.0Cl-2	2.1	763	12.17	2.99E-04
PbB(OH)4-3.0Cl-1	3.2	763	12.24	1.89E-04
PbB(OH)4-3.0Cl-2	3.2	763	12.24	3.05E-04
PbB(OH)4-4.0Cl-1	4.4	763	12.33	1.83E-04
PbB(OH)4-4.0Cl-2	4.4	763	12.31	1.84E-04
PbB(OH)4-5.0Cl-1	5.0	763	12.34	1.67E-04
PbB(OH)4-5.0Cl-2	5.0	763	12.33	1.46E-04
PbB(OH)4-0.01Cl-1	0.010	1457	11.69	4.42E-04
PbB(OH)4-0.01Cl-2	0.010	1457	11.64	4.21E-04
PbB(OH)4-0.1Cl-1	0.10	1457	11.94	5.42E-04
PbB(OH)4-0.1Cl-2	0.10	1457	11.89	5.31E-04
PbB(OH)4-1.0Cl-1	1.0	1457	11.87	3.17E-04
PbB(OH)4-1.0Cl-2	1.0	1457	11.85	3.06E-04
PbB(OH)4-2.0Cl-1	2.1	1457	12.03	2.99E-04
PbB(OH)4-2.0Cl-2	2.1	1457	11.92	2.28E-04
PbB(OH)4-3.0Cl-1	3.2	1457	12.01	1.83E-04
PbB(OH)4-3.0Cl-2	3.2	1457	12.00	2.13E-04
PbB(OH)4-4.0Cl-1	4.4	1457	12.12	1.57E-04
PbB(OH)4-4.0Cl-2	4.4	1457	12.13	1.86E-04
PbB(OH)4-5.0Cl-1	5.0	1457	12.12	1.49E-04
PbB(OH)4-5.0Cl-2	5.0	1457	12.12	1.41E-04

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434 \* Values of pmH reported are calculated by using the correction factors ( $A_M$ ) from Rai  
435 et al. (1995) for pH readings, and conversion factors ( $\Theta$ ) from molarity to molality, pmH  
436 =  $\text{pH}_{\text{ob}} + A_M - \log \Theta$  (Xiong et al., 2010). The conversion factors are calculated from  
437 densities for NaCl solutions, which are from Söhnel and Novotný (1985).  
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Table 3. Experimental results concerning solubility of litharge,  $\alpha$ -PbO(cr), in Na<sub>2</sub>SO<sub>4</sub> solutions in the presence of 0.001 mol•kg<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub> produced at SNL at 22.5 ± 0.5 °C.

Experimental Number	Supporting Medium, Na <sub>2</sub> SO <sub>4</sub> , mol•kg <sup>-1</sup>	Experimental time, days	pmH*	Solubility expressed as total lead on molal scale, m <sub>ΣPb</sub>
PbB(OH)4-0.01SO4-1	0.010	162	11.33	3.03E-04
PbB(OH)4-0.01SO4-2	0.010	162	11.35	3.06E-04
PbB(OH)4-0.1SO4-1	0.10	162	11.68	6.50E-04
PbB(OH)4-0.1SO4-2	0.10	162	11.71	6.73E-04
PbB(OH)4-0.5SO4-1	0.50	162	11.59	6.07E-04
PbB(OH)4-0.5SO4-2	0.50	162	11.62	5.70E-04
PbB(OH)4-1.0SO4-1	1.0	162	11.51	3.95E-04
PbB(OH)4-1.0SO4-2	1.0	162	11.41	3.60E-04
PbB(OH)4-1.5SO4-1	1.5	162	11.48	3.52E-04
PbB(OH)4-1.5SO4-2	1.5	162	11.52	3.62E-04
PbB(OH)4-1.8SO4-1	1.8	162	11.61	3.88E-04
PbB(OH)4-1.8SO4-2	1.8	162	11.63	3.80E-04
PbB(OH)4-0.01SO4-1	0.010	253	11.47	3.02E-04
PbB(OH)4-0.01SO4-2	0.010	253	11.44	3.06E-04
PbB(OH)4-0.1SO4-1	0.10	253	11.66	6.39E-04
PbB(OH)4-0.1SO4-2	0.10	253	11.68	6.87E-04
PbB(OH)4-0.5SO4-1	0.50	253	11.56	6.83E-04
PbB(OH)4-0.5SO4-2	0.50	253	11.49	6.22E-04
PbB(OH)4-1.0SO4-1	1.0	253	11.43	5.34E-04
PbB(OH)4-1.0SO4-2	1.0	253	11.49	5.26E-04
PbB(OH)4-1.5SO4-1	1.5	253	11.51	5.31E-04
PbB(OH)4-1.5SO4-2	1.5	253	11.57	5.43E-04
PbB(OH)4-1.8SO4-1	1.8	253	11.68	5.24E-04
PbB(OH)4-1.8SO4-2	1.8	253	11.60	5.56E-04
PbB(OH)4-0.01SO4-1	0.010	302	11.48	2.93E-04
PbB(OH)4-0.01SO4-2	0.010	302	11.50	3.02E-04
PbB(OH)4-0.1SO4-1	0.10	302	11.75	6.86E-04
PbB(OH)4-0.1SO4-2	0.10	302	11.75	6.60E-04
PbB(OH)4-0.5SO4-1	0.50	302	11.64	6.51E-04
PbB(OH)4-0.5SO4-2	0.50	302	11.57	6.05E-04

PbB(OH)4-1.0SO4-1	1.0	302	11.49	4.83E-04
PbB(OH)4-1.0SO4-2	1.0	302	11.52	4.62E-04
PbB(OH)4-1.5SO4-1	1.5	302	11.51	4.32E-04
PbB(OH)4-1.5SO4-2	1.5	302	11.66	4.69E-04
PbB(OH)4-1.8SO4-1	1.8	302	11.66	4.65E-04
PbB(OH)4-1.8SO4-2	1.8	302	11.66	4.54E-04
PbB(OH)4-0.01SO4-1	0.010	350	11.49	3.10E-04
PbB(OH)4-0.01SO4-2	0.010	350	11.49	3.14E-04
PbB(OH)4-0.1SO4-1	0.10	350	11.72	6.36E-04
PbB(OH)4-0.1SO4-2	0.10	350	11.69	6.81E-04
PbB(OH)4-0.5SO4-1	0.50	350	11.53	7.06E-04
PbB(OH)4-0.5SO4-2	0.50	350	11.48	6.54E-04
PbB(OH)4-1.0SO4-1	1.0	350	11.35	5.54E-04
PbB(OH)4-1.0SO4-2	1.0	350	11.34	5.61E-04
PbB(OH)4-1.5SO4-1	1.5	350	11.38	5.06E-04
PbB(OH)4-1.5SO4-2	1.5	350	11.44	5.39E-04
PbB(OH)4-1.8SO4-1	1.8	350	11.45	5.11E-04
PbB(OH)4-1.8SO4-2	1.8	350	11.44	5.34E-04
PbB(OH)4-0.01SO4-1	0.010	400	11.46	3.08E-04
PbB(OH)4-0.01SO4-2	0.010	400	11.50	3.13E-04
PbB(OH)4-0.1SO4-1	0.10	400	11.68	6.95E-04
PbB(OH)4-0.1SO4-2	0.10	400	11.72	6.64E-04
PbB(OH)4-0.5SO4-1	0.50	400	11.50	6.77E-04
PbB(OH)4-0.5SO4-2	0.50	400	11.47	6.41E-04
PbB(OH)4-1.0SO4-1	1.0	400	11.31	5.68E-04
PbB(OH)4-1.0SO4-2	1.0	400	11.23	5.66E-04
PbB(OH)4-1.5SO4-1	1.5	400	11.37	5.11E-04
PbB(OH)4-1.5SO4-2	1.5	400	11.38	5.56E-04
PbB(OH)4-1.8SO4-1	1.8	400	11.44	5.17E-04
PbB(OH)4-1.8SO4-2	1.8	400	11.39	5.20E-04
PbB(OH)4-0.01SO4-1	0.010	551	11.50	3.02E-04
PbB(OH)4-0.01SO4-2	0.010	551	11.51	3.05E-04
PbB(OH)4-0.1SO4-1	0.10	551	11.75	7.07E-04
PbB(OH)4-0.1SO4-2	0.10	551	11.69	5.40E-04
PbB(OH)4-0.5SO4-1	0.50	551	11.59	6.90E-04
PbB(OH)4-0.5SO4-2	0.50	551	11.57	5.97E-04
PbB(OH)4-1.0SO4-1	1.0	551	11.51	5.49E-04

PbB(OH)4-1.0SO4-2	1.0	551	11.46	5.52E-04
PbB(OH)4-1.5SO4-1	1.5	551	11.54	5.31E-04
PbB(OH)4-1.5SO4-2	1.5	551	11.57	5.38E-04
PbB(OH)4-1.8SO4-1	1.8	551	11.64	5.37E-04
PbB(OH)4-1.8SO4-2	1.8	551	11.63	5.35E-04
PbB(OH)4-0.01SO4-1	0.010	611	11.51	2.97E-04
PbB(OH)4-0.01SO4-2	0.010	611	11.50	3.13E-04
PbB(OH)4-0.1SO4-1	0.10	611	11.73	7.03E-04
PbB(OH)4-0.1SO4-2	0.10	611	11.63	4.96E-04
PbB(OH)4-0.5SO4-1	0.50	611	11.51	7.35E-04
PbB(OH)4-0.5SO4-2	0.50	611	11.49	6.11E-04
PbB(OH)4-1.0SO4-1	1.0	611	11.39	5.48E-04
PbB(OH)4-1.0SO4-2	1.0	611	11.41	5.36E-04
PbB(OH)4-1.5SO4-1	1.5	611	11.42	5.23E-04
PbB(OH)4-1.5SO4-2	1.5	611	11.53	5.35E-04
PbB(OH)4-1.8SO4-1	1.8	611	11.51	5.05E-04
PbB(OH)4-1.8SO4-2	1.8	611	11.51	5.32E-04
PbB(OH)4-0.01SO4-1	0.010	695	11.47	3.15E-04
PbB(OH)4-0.01SO4-2	0.010	695	11.49	3.09E-04
PbB(OH)4-0.1SO4-1	0.10	695	11.68	7.14E-04
PbB(OH)4-0.1SO4-2	0.10	695	11.60	5.21E-04
PbB(OH)4-0.5SO4-1	0.50	695	11.51	6.96E-04
PbB(OH)4-0.5SO4-2	0.50	695	11.48	9.37E-04
PbB(OH)4-1.0SO4-1	1.0	695	11.35	5.70E-04
PbB(OH)4-1.0SO4-2	1.0	695	11.36	5.41E-04
PbB(OH)4-1.5SO4-1	1.5	695	11.37	4.96E-04
PbB(OH)4-1.5SO4-2	1.5	695	11.37	5.15E-04
PbB(OH)4-1.8SO4-1	1.8	695	11.42	5.03E-04
PbB(OH)4-1.8SO4-2	1.8	695	11.41	5.22E-04
PbB(OH)4-0.01SO4-1	0.010	1461	11.09	2.79E-04
PbB(OH)4-0.01SO4-2	0.010	1461	11.25	2.90E-04
PbB(OH)4-0.1SO4-1	0.10	1461	11.36	4.43E-04
PbB(OH)4-0.1SO4-2	0.10	1461	11.38	4.74E-04
PbB(OH)4-0.5SO4-1	0.50	1461	11.31	6.59E-04
PbB(OH)4-0.5SO4-2	0.50	1461	11.23	5.57E-04
PbB(OH)4-1.0SO4-1	1.0	1461	11.09	4.90E-04

PbB(OH)4-1.0SO4-2	1.0	1461	11.08	5.05E-04
PbB(OH)4-1.5SO4-1	1.5	1461	11.08	4.32E-04
PbB(OH)4-1.5SO4-2	1.5	1461	11.07	4.33E-04
PbB(OH)4-1.8SO4-1	1.8	1461	11.12	4.91E-04
PbB(OH)4-1.8SO4-2	1.8	1461	11.16	5.30E-04

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444 \* Values of pmH reported are calculated by using the correction factors ( $A_M$ ) from  
445 Roselle (2011) for pH readings, and conversion factors ( $\Theta$ ) from molarity to molality,  
446  $\text{pmH} = \text{pH}_{\text{ob}} + A_M - \log \Theta$  (Xiong et al., 2010). The conversion factors are calculated  
447 from densities for  $\text{Na}_2\text{SO}_4$  solutions, which are from Söhnel and Novotný (1985).  
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Table 4. Equilibrium constants at infinite dilution, 25°C and 1 bar, Pitzer interaction parameters in the  $\text{Na}^+ - \text{Pb}^{2+} - \text{Cl}^- - \text{ClO}_4^- - \text{SO}_4^{2-}$  system

Pitzer Parameters					
Species, <i>i</i>	Species, <i>j</i>	$\beta^{(0)}$	$\beta^{(1), \text{A}}$	$C^\phi$	References
$\text{Na}^+$	$\text{Pb}(\text{OH})_3^-$	0.3354	0.29	0	This work
$\text{PbOH}^+$	$\text{ClO}_4^-$	0	0	0	This work
$\text{PbOH}^+$	$\text{Cl}^-$	0	0	0	This work
$\text{Na}^+$	$\text{PbCl}_3^-$	-0.0605	0	0.091	Xiong (2013a)
Pitzer Mixing Interaction Parameters and Interaction Parameters Involving Neutral Species					
Species <i>i</i>	Species <i>j</i>	Species <i>k</i>	$\theta_{ij}$	$\psi_{ijk}$	References
$\text{ClO}_4^-$	$\text{Pb}(\text{OH})_2(\text{aq})$		0		This work
$\text{Cl}^-$	$\text{Pb}(\text{OH})_2(\text{aq})$		-0.1721		This work
$\text{Na}^+$	$\text{Pb}(\text{OH})_2(\text{aq})$		0		This work
$\text{SO}_4^{2-}$	$\text{Pb}(\text{OH})_2(\text{aq})$		-0.5581		This work
$\text{SO}_4^{2-}$	$\text{Pb}(\text{OH})_3^-$		-0.4046		This work
$\text{Na}^+$	$\text{PbCl}_2(\text{aq})$		-0.11		Felmy et al. (2000)
$\text{Cl}^-$	$\text{PbCl}_3^-$		0		This work
$\text{Na}^+$	$\text{Pb}^{2+}$		0.10		Felmy et al. (2000)
$\text{Na}^+$	$\text{PbCl}_2(\text{aq})$	$\text{Cl}^-$		0	Xiong (2013a)
Equilibrium Constants for Dissolution Reaction of Litharge and Formation Reactions for Lead Hydroxyl Species					
Reaction			$\log K_{sp}$ and $\log \beta_1$ , $\log \beta_2$ , $\log \beta_3$ at 25 °C		References
$\text{PbO}(\text{cr}) + 2\text{H}^+ \rightleftharpoons \text{Pb}^{2+} + \text{H}_2\text{O}(\text{l})$			12.59		Data0.ymp.R2 (Wolery & Jarek, 2003)*
$\text{Pb}^{2+} + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{PbOH}^+ + \text{H}^+$			-7.46		Powell et al. (2009)
$\text{Pb}^{2+} + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Pb}(\text{OH})_2(\text{aq}) + 2\text{H}^+$			-17.05		This work
$\text{Pb}^{2+} + 3\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Pb}(\text{OH})_3^- + 3\text{H}^+$			-27.99		This work

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<sup>A</sup> Values are set according to AP-154, Revision 2 (Xiong, 2013b).

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459 Figure Captions

460

461 Figure 1. A plot showing experimental total lead concentrations in equilibrium with  
462 litharge,  $\alpha$ -PbO(cr), in NaClO<sub>4</sub> solutions as a function of experimental time produced in  
463 this study.

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465

466 Figure 2. A plot showing experimental total calcium concentrations in equilibrium with  
467 litharge,  $\alpha$ -PbO(cr), in NaCl solutions as a function of experimental time produced in this  
468 study.

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471 Figure 3. A plot showing experimental total lead concentrations in equilibrium with  
472 litharge,  $\alpha$ -PbO(cr), in Na<sub>2</sub>SO<sub>4</sub> solutions as a function of experimental time produced in  
473 this study.

474

475 Figure 4. A plot showing comparisons of model-predicted solubilities with experimental  
476 total lead concentrations, in equilibrium with litharge,  $\alpha$ -PbO(cr), in NaClO<sub>4</sub> solutions as  
477 a function of negative logarithms of hydrogen ion concentrations on a molal scale, pH<sub>m</sub>.

478

479 Figure 5. A plot showing comparisons of model-predicted solubilities with experimental  
480 total lead concentrations, in equilibrium with litharge,  $\alpha$ -PbO(cr), in NaCl solutions  
481 ranging from 0.01 to 1.0 mol•kg<sup>-1</sup> as a function of negative logarithms of hydrogen ion  
482 concentrations on a molal scale, pH<sub>m</sub>.

483

484 Figure 6. A plot showing comparisons of model-predicted solubilities with experimental  
485 total lead concentrations, in equilibrium with litharge,  $\alpha$ -PbO(cr), in NaCl solutions  
486 ranging from 2.1 to 5.6 mol•kg<sup>-1</sup> as a function of negative logarithms of hydrogen ion  
487 concentrations on a molal scale, pH<sub>m</sub>.

488

489 Figure 7. A plot showing comparisons of model-predicted solubilities with experimental  
490 total lead concentrations, in equilibrium with litharge,  $\alpha$ -PbO(cr), in Na<sub>2</sub>SO<sub>4</sub> solutions  
491 ranging from 0.01 to 0.5 mol•kg<sup>-1</sup> as a function of negative logarithms of hydrogen ion  
492 concentrations on a molal scale, pH<sub>m</sub>.

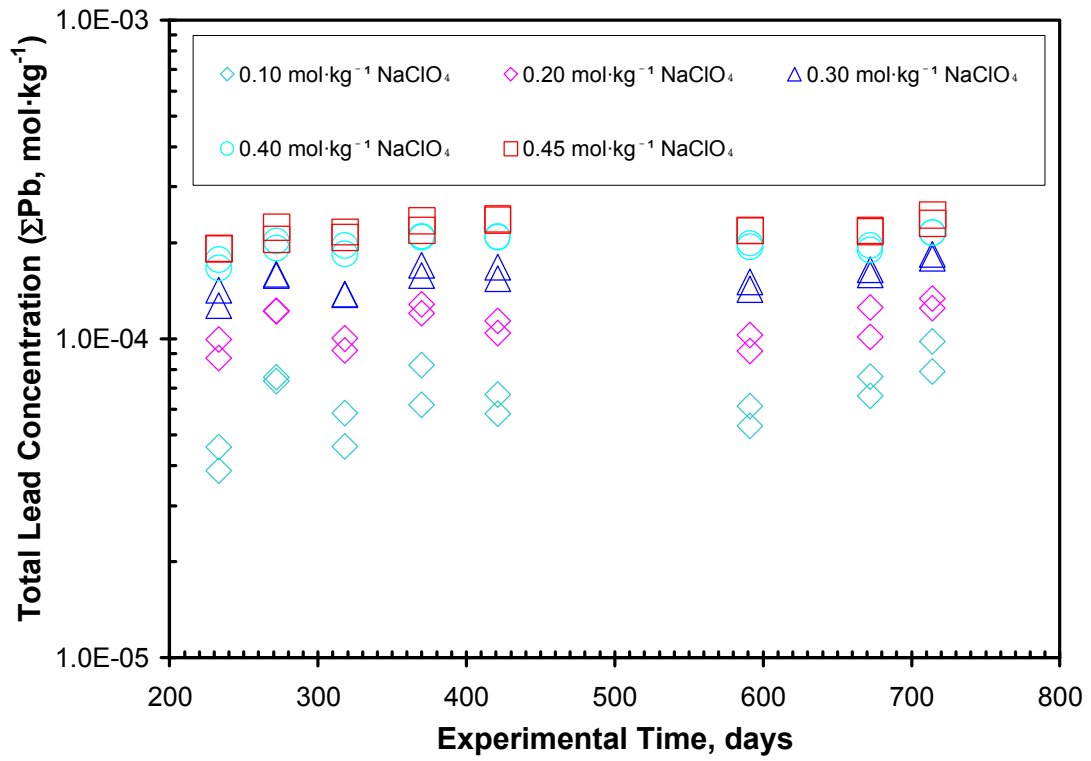
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494 Figure 8. A plot showing comparisons of model-predicted solubilities with experimental  
495 total lead concentrations, in equilibrium with litharge,  $\alpha$ -PbO(cr), in Na<sub>2</sub>SO<sub>4</sub> solutions  
496 ranging from 1.0 to 1.8 mol•kg<sup>-1</sup> as a function of negative logarithms of hydrogen ion  
497 concentrations on a molal scale, pH<sub>m</sub>.

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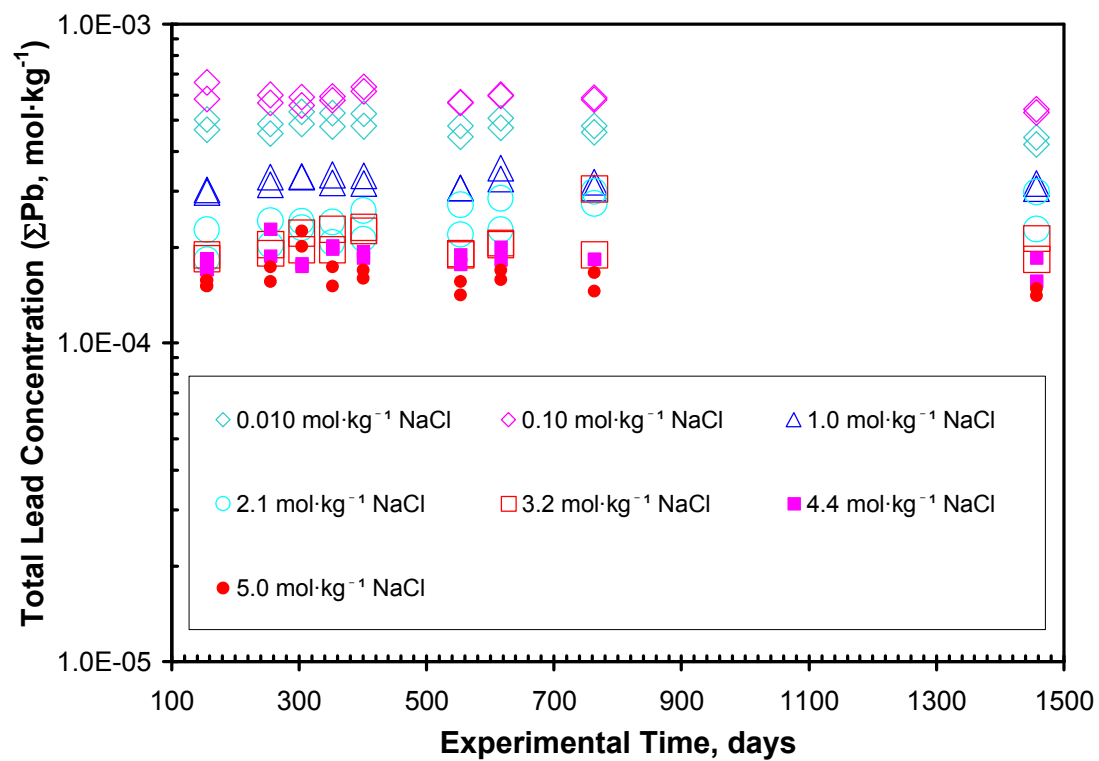


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Figure 1.



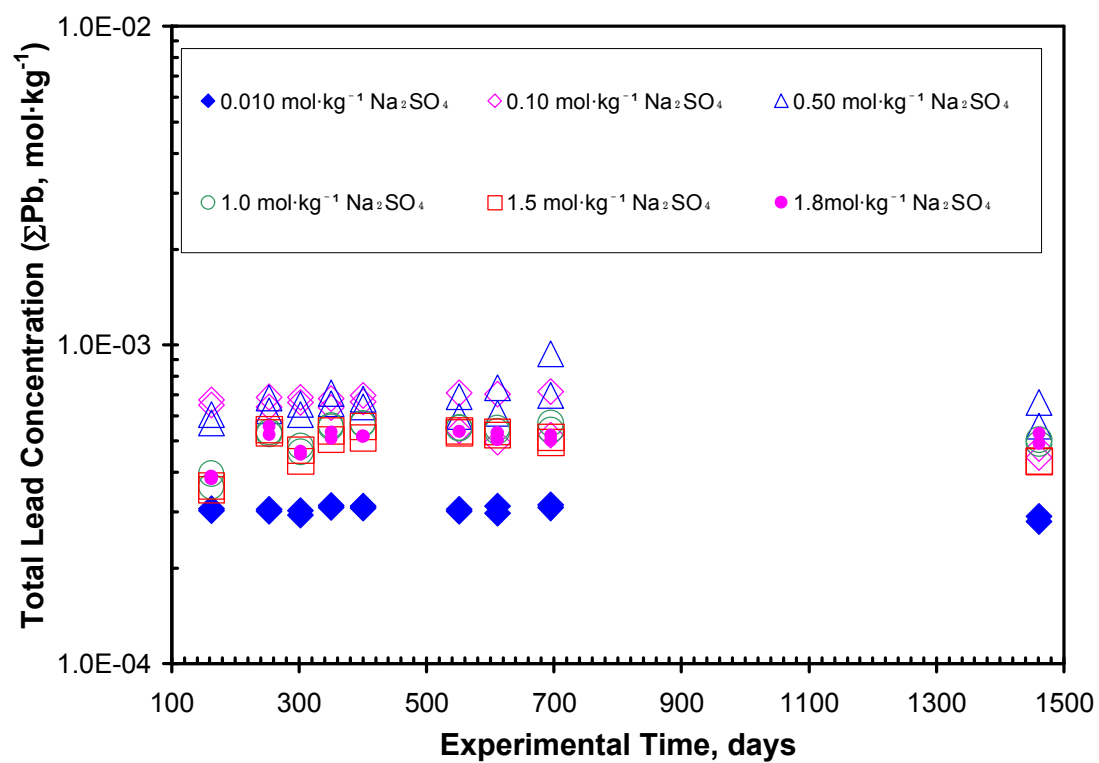
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Figure 2.

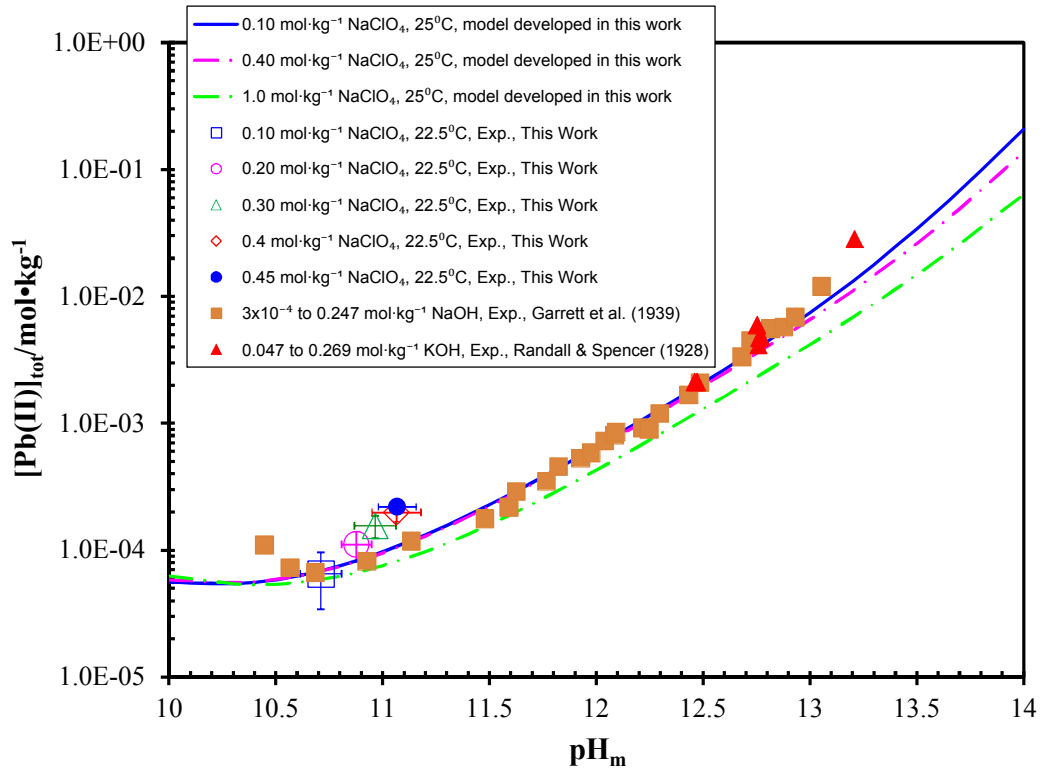
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Figure 3.

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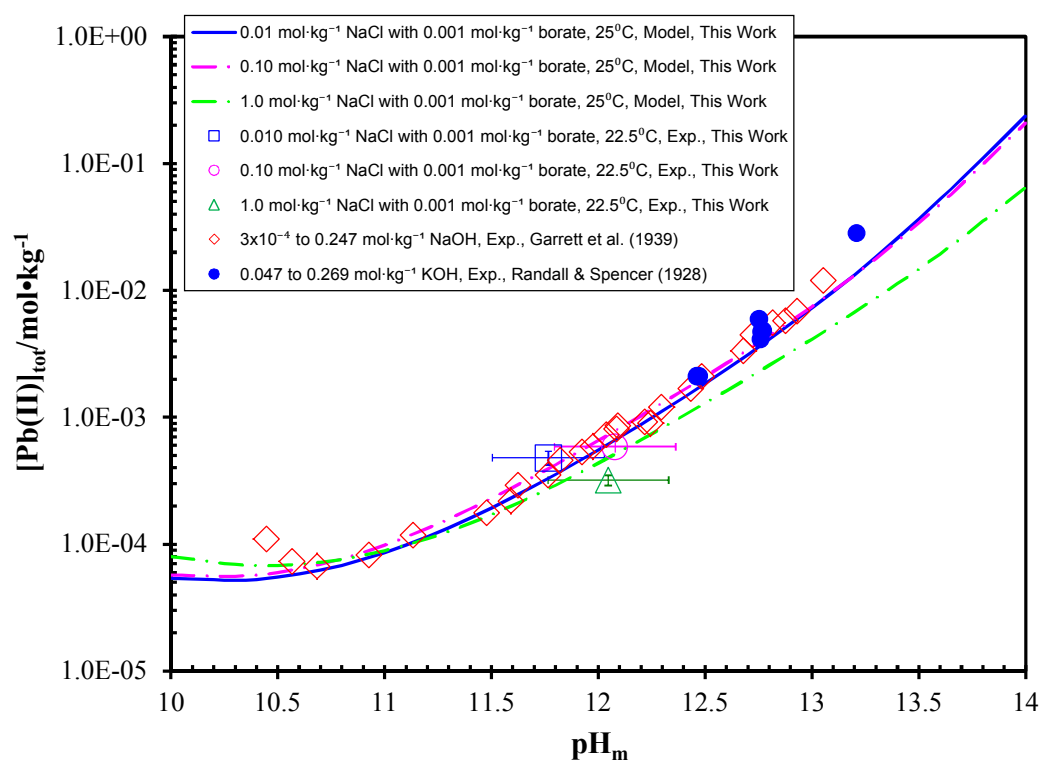
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524 Figure 4.

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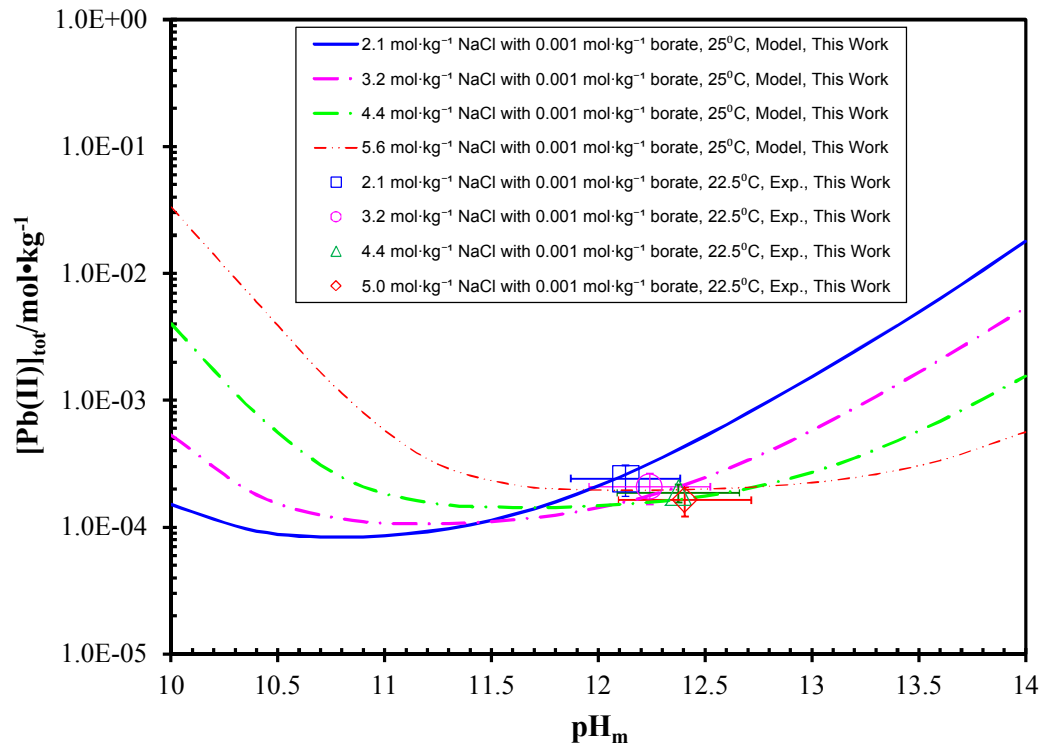
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530 Figure 5.

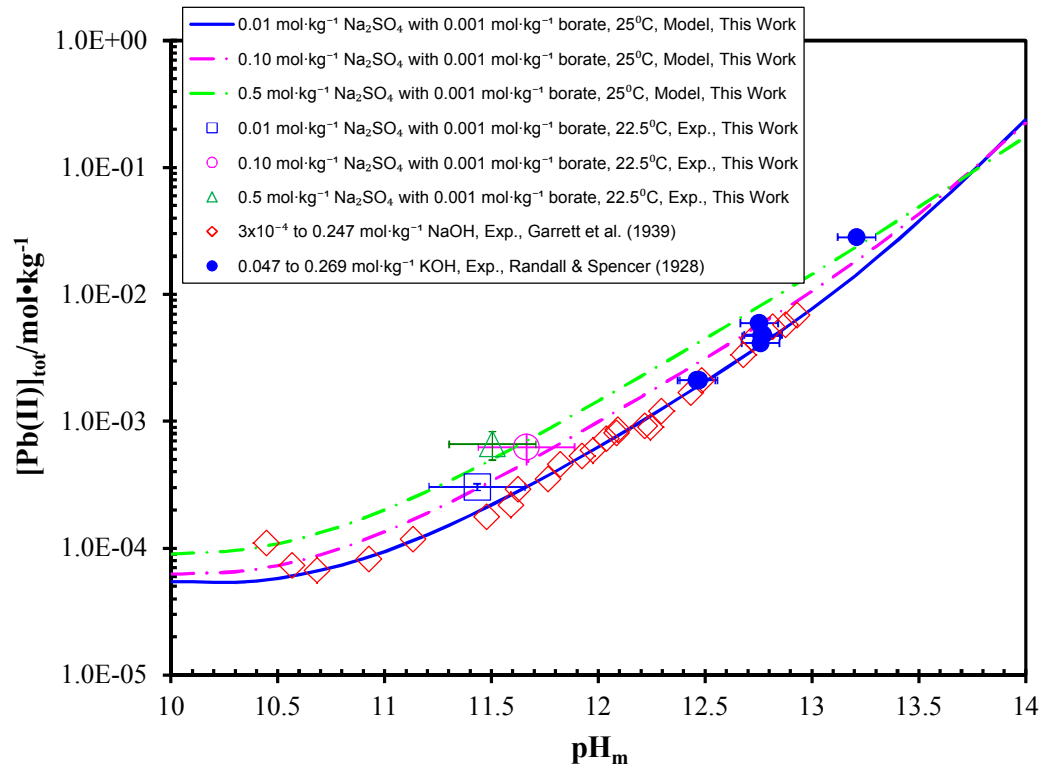
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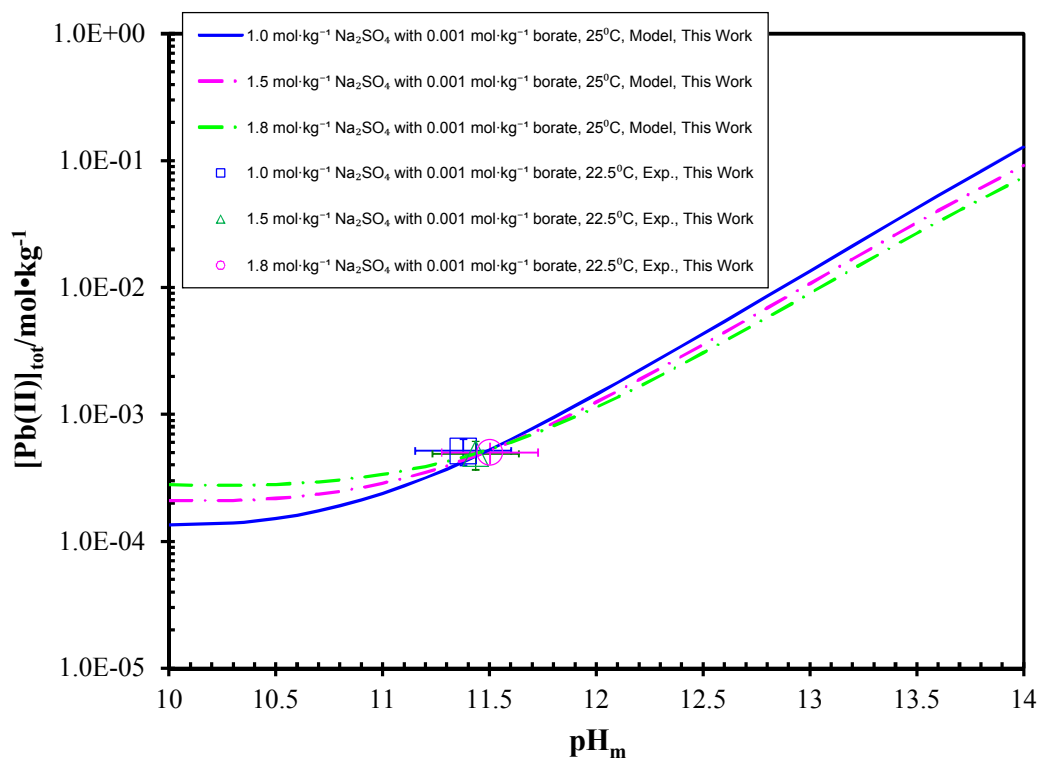
Figure 6.



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Figure 7.

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Figure 8.