

1 Experimental determination of solubilities of lead oxalate
2 (PbC₂O₄(cr)) in a NaCl medium to high ionic strengths, and the
3 importance of lead oxalate in low temperature environments
4

5 Yongliang Xiong^{1,*}, Leslie Kirkes^{*}, Terry Westfall^{*}, Taya Olivas^{*},
6 and Rachael Roselle^{**}

7 *Sandia National Laboratories (SNL)
8 Carlsbad Programs Group
9 4100 National Parks Highway, Carlsbad, NM 88220, USA
10

10

11

12 **Department of German Studies and Slavic Languages
13 Brigham Young University, Provo UT 84602-6119
14

14

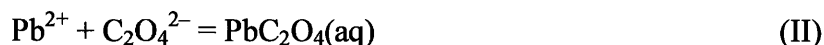
15

¹ Corresponding author, e-mail: yxiong@sandia.gov.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24

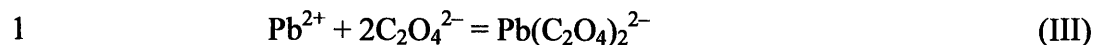
ABSTRACT

In this study, the solubility product constant ($\log K_{sp}$) for lead oxalate ($\text{PbC}_2\text{O}_4(\text{cr})$) pertaining to Reaction (I), and the formation constant of $\text{PbC}_2\text{O}_4(\text{aq})$ ($\log \beta_1$) pertaining to Reaction (II)



at infinite dilution, 25 °C and 1 bar, are determined as -11.13 ± 0.10 (2σ) and 5.85 ± 0.10 (2σ) in logarithmic units, respectively, based on solubility data for $\text{PbC}_2\text{O}_4(\text{cr})$ in NaCl solutions up to 5.0 m evaluated using the Pitzer model. The above solubility product constant determined in this study is significantly lower than the value of -10.50 ± 0.29 (2σ) for $\log K_{sp}$, based on the evaluation of literature solubility data using the Brønsted-Guggenheim-Scatchard specific interaction theory (SIT) model (also derived in this study). The above $\log \beta_1$ determined in this study agrees within the quoted uncertainties with the value of 5.39 ± 0.38 (2σ) derived in this study from the literature data using the SIT model.

In addition, based on solubility data for $\text{PbC}_2\text{O}_4(\text{cr})$ in a $\text{K}_2\text{C}_2\text{O}_4$ medium up to 0.5 M at $25 \pm 2^\circ\text{C}$ from the literature, this study also derives $\log \beta_2$ for the following reaction by using the Pitzer model,



2

3 as 8.05 ± 0.07 (2σ). In combination with the above $\log K_{\text{sp}} = -11.13 \pm 0.10$ (2σ) and
4 $\log \beta_1 = 5.85 \pm 0.10$ (2σ), the model with $\log \beta_2 = 8.05 \pm 0.07$ (2σ) well reproduces
5 solubilities of $\text{PbC}_2\text{O}_4(\text{cr})$ in a $\text{K}_2\text{C}_2\text{O}_4$ medium up to 0.5 M.

6

7 INTRODUCTION

8 Recent studies have indicated that pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$), believed to be the
9 most stable lead mineral under the Earth's surface conditions, can be transformed to lead
10 oxalate by saprotrophic and mycorrhizal fungi (e.g., Sayer et al., 1999; Fomina et al.,
11 2004; 2005; 2007). It was noted that *Aspergillus niger*, a fungus, and one of the most
12 common species of the genus *Aspergillus*, first transformed pyromorphite into lead
13 oxalate dihydrate, which then becomes anhydrous lead oxalate. In this process,
14 *Aspergillus niger* extracts the phosphate and precipitates almost all of the lead as lead
15 oxalate. In addition, the formation of lead oxalate on the surface of galena via the fungi
16 weathering of galena is also observed (Adeyemi and Gadd, 2005). The formation of lead
17 oxalate could be an important mechanism in immobilization of lead in environments near
18 the Earth's surface (Gadd, 2000), making lead oxalate ($\text{PbC}_2\text{O}_4(\text{cr})$) an important lead
19 phase in soils, and possibly a source-term phase for lead in low temperature
20 environments.

21 In the field of nuclear waste isolation, crystalline lead oxalate and aqueous lead
22 complexes are important. Crystalline lead oxalate could be a potentially important
23 solubility-limiting phase for lead, oxalate, or both. Aqueous lead complexes can compete

1 with actinides for dissolved oxalate in complexation, lowering the total soluble fraction
2 of actinides. When oxalate is present in actinide waste-streams without competitor(s) for
3 soluble oxalate, complexation of actinides with oxalate would increase solubilities of
4 actinides, making them more transportable. However, if lead is used as a radiation-
5 shielding material for wastes with significant γ -radiation, the dissolved lead ion (Pb^{2+})
6 can form strong complex(es) with oxalate, making Pb^{2+} a strong competitor for soluble
7 oxalate. This lessens the impact that complexation of actinides with oxalate has on the
8 transportable concentrations of actinides in a waste stream. In the Waste Isolation Pilot
9 Plant (WIPP), a U.S. Department of Energy geological repository for the permanent
10 disposal of defense-related transuranic (TRU) waste, there are significant inventories of
11 oxalate in the waste-stream. For example, the oxalate concentration for the 2009
12 Compliance Re-certification Application Performance Assessment Baseline Calculations
13 (CRA-2009 PABC) for the WIPP, is 1.7×10^{-2} M (Brush and Xiong, 2009).

14 There are a few earlier solubility studies on PbC_2O_4 (cr). Kolthoff et al. (1942)
15 investigated the solubility of PbC_2O_4 (cr) in $\text{K}_2\text{C}_2\text{O}_4$ solutions up to 0.5 M. In the study
16 of Klatt (1970), the author measured solubilities of PbC_2O_4 (cr) in KNO_3 solutions up to
17 1.5 M. In the study of Hedstrom et al. (1977), these authors determined the solubility of
18 PbC_2O_4 (cr) in a 1 M NaClO_4 solution. While these studies provide valuable information
19 regarding solubilities of PbC_2O_4 (cr) in various media relevant to laboratory conditions,
20 they are not of much relevance to natural environments, as natural environments are
21 usually dominated by NaCl media and lead will form aqueous complexes with chloride in
22 such media. At the WIPP, there are brines that are important to the Performance
23 Assessment (PA), i.e., ERDA-6, a Na-Cl dominated brine, and GWB, a Na-Mg-Cl

1 dominated brine (Popielak et al., 1983; U.S. DOE, 2004, Appendix BARRIERS; Xiong
2 and Lord, 2008). In the WIPP brines, the concentrations of Na and Cl are 4.04 m and
3 6.40 m for GWB, and 5.35 m and 5.27 m for ERDA-6, respectively (Xiong and Lord,
4 2008, and references therein). Therefore, investigation of the solubility of PbC_2O_4 (cr) in
5 a NaCl media is important for many applications.

6
7

8 EXPERIMENTAL METHODS

9

10 In our solubility experiments, about 0.5 grams of the solubility controlling
11 material, lead oxalate (purity 99.999%) from Alfa Aesar, were weighed out and placed
12 into 150 mL plastic bottles. 100 mL of various supporting solutions were added to the
13 bottles. Once filled, the lids of the bottles were sealed with parafilm. The supporting
14 electrolytes are a series of NaCl solutions ranging from 0.010 m to 5.0 m. The NaCl
15 solutions except the one at 5.0 m were originally prepared on molar scale, and they were
16 converted to molal scale by using the densities for NaCl solutions from Söhnel and
17 Novotný (1985). Undersaturation experiments were conducted at the laboratory room
18 temperature ($22.5 \pm 1.5^\circ\text{C}$).

19 The pH was measured with an Orion-Ross combination pH glass electrode, using
20 a pH meter that was calibrated with three pH buffers (pH 4, pH 7, and pH 10). In
21 solutions with an ionic strength higher than 0.10 m, hydrogen-ion concentrations (pCH)
22 were determined from observed pH values measured with the pH glass electrode by
23 applying correction factors, as detailed in Xiong (2008) and Xiong and Lord (2008). In
24 Xiong et al. (2010a), a detailed procedure to obtain similar correction factors is provided.

1 Lead concentrations of solutions were analyzed with a Perkin Elmer dual-view
2 inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Perkin Elmer DV
3 3300). Calibration blanks and standards were precisely matched with experimental
4 matrices. The linear correlation coefficients for the calibration curves in all
5 measurements were better than 0.9995. The analytical precision for ICP-AES is better
6 than 1.00% in terms of the relative standard deviation (RSD) based on replicate analyses.
7 Oxalate concentrations of solutions were analyzed with a DIONEX ion chromatograph
8 (IC) (DIONEX IC 3000). The linear correlation coefficients for the calibration curves in
9 all measurements using the IC were better than 0.9994. The analytical precision for IC is
10 usually better than 3.00% in terms of RSD for samples with low concentration of NaCl
11 matrixes based on replicate analyses. Because the IC columns have issues with high
12 concentrations of matrix solutions over loading the column, oxalate concentrations in
13 experiments with high concentrations of NaCl have high experimental errors and are not
14 used. Total lead concentrations ($m_{\Sigma\text{Pb}}$) are reported as solubilities of $\text{PbC}_2\text{O}_4(\text{cr})$.

15 Solid phase was analyzed using a Bruker D8 Advance X-ray diffractometer with a
16 Sol-X detector. There was no phase change during the experiments.

17

18 EXPERIMENTAL RESULTS, INTERPRETATIONS AND DISCUSSIONS

19

20 As mentioned in Experimental Methods, oxalate concentrations in experiments
21 with 0.010 m and 0.10 m NaCl solutions are usually below the detection limit of the IC
22 and oxalate concentrations in experiments with high matrix NaCl have large experimental
23 errors. In contrast, ICP-AES data for lead are more precise, and are detectable in all
24 experiments. Therefore, solubilities of $\text{PbC}_2\text{O}_4(\text{cr})$ are represented by total lead

1 concentrations (Table 1), and they are employed in computer modeling (see below). In
2 Table 1 and Figure 1, solubilities of PbC_2O_4 (cr) as a function of molality of NaCl are
3 presented. It is clear from Table 1 and Figure 1 that solubilities of PbC_2O_4 (cr) have a
4 strong dependence on molalities of NaCl; i.e., solubilities of PbC_2O_4 (cr) increase with
5 increasing molalities of NaCl.

6 In the following, experimental results are employed to determine the solubility
7 product constant (K_{sp}) of PbC_2O_4 (cr) and the stability constant (β_I) of PbC_2O_4 (aq) by
8 using the Pitzer model to fit experimental data. In addition, literature values are also
9 reviewed.

10 In this study, the standard state for a solid phase is defined as its pure end-member
11 at 298.15 K and 1 bar. The standard state of an aqueous solute is defined as a
12 hypothetical 1 molal solution at 298.15 K and 1 bar. The reference state of an aqueous
13 solute is at infinite dilution whereby the activity approaches the molal concentration
14 (Nordstrom and Munoz, 1986).

15 As our experiments are in NaCl media, complexation of Pb^{2+} with Cl^- needs to be
16 considered in modeling our experimental results. It is well known that Pb^{2+} forms several
17 aqueous complexes with Cl^- (Millero and Byrne, 1984; Luo and Millero, 2007; Powell et
18 al., 2009) (Table 2). The work of Millero and Byrne (1984) used the Pitzer model to
19 extrapolate formation constants of lead-chloride complexes to infinite dilution. In the
20 review performed by Powell et al. (2009), the authors employed the Brønsted-
21 Guggenheim-Scatchard specific interaction theory (SIT) model for extrapolation to
22 infinite dilution. From Table 2, it is obvious that the recommended values from these
23 two studies are in good agreement. For sake of consistency with the Pitzer model used in

1 this study, the values from Millero and Byrne (1984) are adopted in this study for
2 modeling. In the above two studies, PbCl_4^{2-} was not present. Felmy et al. (2000)
3 suggested a value of 0.14 for $\log \beta_4$ of PbCl_4^{2-} . In the valuation of Powell et al. (2009),
4 the authors concluded that the results at present are conflicting regarding the presence of
5 PbCl_4^{2-} . Therefore, PbCl_4^{2-} is not included in the present model.

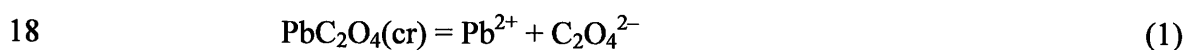
6 In Table 2, Pitzer parameters adopted in the geochemical model are also
7 tabulated. The computer modeling is performed by using EQ3/6 version 8.0a (Wolery et
8 al., 2010; Xiong, 2011). The essence of the modeling is to minimize the difference
9 between experimental and model predicted values, as detailed in our previous publication
10 (Nemer et al., 2011). Unless otherwise noted, uncertainties presented in this study are
11 two standard deviations (2σ).

12

13 *Solubility Product Constant for $\text{PbC}_2\text{O}_4(\text{cr})$*

14 In the solubility study of Hedström et al. (1977), the authors determined the
15 solubility product constant ($\log Q_{sp}$) of lead oxalate in 1.0 M NaClO_4 at 25°C as
16 -9.02 ± 0.14 for the following reaction,

17



19

20 In this study, the above solubility product constant at 1.0 M ionic strength is extrapolated
21 to infinite dilution by using the SIT model,

22

$$23 \quad \log K_{sp} = \log Q_{sp} - 8D - \Delta\epsilon \text{ (Eq. 1) } I_m \quad (2)$$

1

$$\Delta\varepsilon \text{ (Eq. 1)} = \varepsilon(\text{Pb}^{2+}, \text{ClO}_4^-) + \varepsilon(\text{Na}^+, \text{C}_2\text{O}_4^{2-}) \quad (3)$$

3

4 In Eq. (2), K_{sp} is the solubility product constant at infinite dilution given by,

5

$$K_{sp} = \frac{a_{\text{Pb}^{2+}} \times a_{\text{C}_2\text{O}_4^{2-}}}{a_{\text{PbC}_2\text{O}_4(\text{cr})}} \quad (4)$$

7

8 where $a_{\text{Pb}^{2+}}$, $a_{\text{C}_2\text{O}_4^{2-}}$, and $a_{\text{PbC}_2\text{O}_4(\text{cr})}$ denote activities of Pb^{2+} , $\text{C}_2\text{O}_4^{2-}$, and $\text{PbC}_2\text{O}_4(\text{cr})$. The

9 activity of $\text{PbC}_2\text{O}_4(\text{cr})$ is taken as unity. Q_{sp} is the solubility product constant at certain

10 ionic strengths, given by the following equation,

11

$$Q_{sp} = m_{\text{Pb}^{2+}} \times m_{\text{C}_2\text{O}_4^{2-}} \quad (5)$$

13

14 where $m_{\text{Pb}^{2+}}$ and $m_{\text{C}_2\text{O}_4^{2-}}$ are molalities of Pb^{2+} and $\text{C}_2\text{O}_4^{2-}$, respectively.

15 In Eq. (2), I_m is ionic strength on molal scale; D is the Debye-Hückel term, given

16 by the following equation,

17

$$D = \frac{A_\gamma \sqrt{I_m}}{1 + 1.5 \times \sqrt{I_m}} \quad (6)$$

19

20 where A_γ is the Debye-Hückel slope for the activity coefficient at the temperature of

21 interest, and is from Helgeson and Kirkham (1974). In Eq. (3), $\varepsilon(\text{Pb}^{2+}, \text{ClO}_4^-)$ and $\varepsilon(\text{Na}^+,$

1 $\text{C}_2\text{O}_4^{2-}$) are the SIT interaction coefficients, which are 0.15 ± 0.02 from Ciavatta (1980)
2 and -0.02 ± 0.05 from Xiong (2009), respectively. The concentration of 1.0 M NaClO_4
3 on the molar scale is converted to molal scale based on the density equation for NaClO_4
4 (Söhnel and Novotný, 1985). Therefore, according to Eq. (2), the $\log K_{sp}$ is computed as
5 -10.53 ± 0.15 .

6 In the study of Klatt et al. (1970), the authors determined solubility product
7 constants in KNO_3 solutions ranging from 0.15 M to 1.5 M. Based on the SIT model, the
8 solubility product constants are extrapolated to infinite dilution (Figure 2) with,

$$10 \quad \Delta\epsilon \text{ (Eq. 1)} = \epsilon(\text{Pb}^{2+}, \text{NO}_3^-) + \epsilon(\text{K}^+, \text{C}_2\text{O}_4^{2-}) \quad (7)$$

11

12 In the extrapolation, the concentrations of KNO_3 on the molar scale are converted to the
13 molal scale based on the density equation for KNO_3 (Söhnel and Novotný, 1985). In the
14 plot, the y-intercept is $\log K_{sp}$, and the slope is $\Delta\epsilon$. Detailed descriptions about using the
15 SIT model to extrapolate to infinite dilution are provided in Grenthe et al. (2000). The
16 $\log K_{sp}$ obtained is -10.38 ± 0.14 . This value is in good agreement with the above value
17 obtained by this study in NaClO_4 media. In addition, based on $\Delta\epsilon \text{ (Eq. 1)} = -0.45 \pm 0.15$,
18 $\epsilon(\text{K}^+, \text{C}_2\text{O}_4^{2-})$ is computed as -0.25 ± 0.19 in accordance with $\epsilon(\text{Pb}^{2+}, \text{NO}_3^-) = -0.20 \pm$
19 0.12 (Table 2).

20 The study of Kubacky-Beard et al. (1996) used an electrochemical cell method in
21 which the solids react with relatively high concentrations of dissolved oxalate. In this
22 method, they relied on the well known Gibbs free energy of formation for
23 $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}(\text{s})$ to determine the Gibbs free energy of formation for $\text{PbC}_2\text{O}_4(\text{cr})$. In

1 combination with the Gibbs free energies of formation for Pb^{2+} and $\text{C}_2\text{O}_4^{2-}$ from Wagman
2 et al. (1982), the $\log K_{sp}$ calculated from the Gibbs free energy of formation for
3 $\text{PbC}_2\text{O}_4(\text{cr})$ determined in their study is -10.58 ± 0.20 .

4 In summary, $\log K_{sp}$ evaluated from literature data ranges from -10.58 to -10.38 .
5 The average value of $\log K_{sp}$ evaluated from literature data would be -10.50 ± 0.29 (Table
6 2).

7 In Figure 1, the dashed line represents predicted solubilities of $\text{PbC}_2\text{O}_4(\text{cr})$ using
8 $\log K_{sp} = -10.50 \pm 0.29$ with $\log \beta_1 = 5.39 \pm 0.38$ evaluated from literature data (see
9 below for details) as a function of molality in NaCl media. It is clear from Figure 1 that
10 the geochemical model with the above $\log K_{sp}$ and $\log \beta_1$ evaluated from the literature
11 data works reasonably well in the ionic strength range from 0.01 m to 0.1 m, but it
12 systematically over-predicts solubilities of $\text{PbC}_2\text{O}_4(\text{cr})$ above ionic strength of 0.1 m.
13 Although the above model over-predicts in the high ionic strength range, it does provide
14 valuable guidance in the modeling of our experimental data to high ionic strengths. In
15 Figure 1, the solid heavy line represents the model with $\log K_{sp} = -11.13 \pm 0.10$ and
16 $\log \beta_1 = 5.85 \pm 0.10$ evaluated from solubility data in NaCl media produced in this study.
17 From Figure 1, it is obvious that this model works well over the entire ionic strength
18 range from 0.01 m to 5.0 m in NaCl media.

19 In addition, Kolthoff et al. (1942) performed solubility experiments on
20 $\text{PbC}_2\text{O}_4(\text{cr})$ in $\text{K}_2\text{C}_2\text{O}_4$ media up to 0.5 M. Their solubility data are also plotted in
21 Figure 1. As their experiments were extended to high concentrations of $\text{C}_2\text{O}_4^{2-}$, $\log \beta_2$ is
22 required. In this study, their experimental data are used to evaluate $\log \beta_2$ (see below for
23 details).

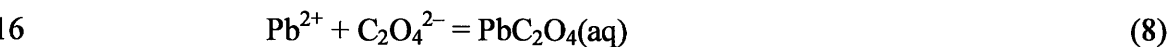
1

2 *Formation Constants for $PbC_2O_4(aq)$ and $Pb(C_2O_4)_2^{2-}$*

3 In the literature, it has been suggested that Pb^{2+} could form two oxalate
4 complexes, i.e., $PbC_2O_4(aq)$ and $Pb(C_2O_4)_2^{2-}$ (e.g., Krishnamurty and Harris, 1961;
5 Hedström et al., 1977). However, Hedström et al. (1977) indicated that Pb^{2+} is
6 overwhelmingly chelated by $C_2O_4^{2-}$ as $PbC_2O_4(aq)$, and $Pb(C_2O_4)_2^{2-}$ does not contribute
7 to the solubility of $PbC_2O_4(cr)$ in solutions with low oxalate concentration. In addition,
8 in the study of Borkowski et al. (2000) on Co^{2+} complexation with oxalate, the authors
9 found that Co^{2+} is also predominantly complexed as $CoC_2O_4(aq)$ at oxalate
10 concentrations lower than 4.0×10^{-3} m. As solubilities of $PbC_2O_4(cr)$ in this study are less
11 than 4.0×10^{-3} m, based on the findings in the above mentioned studies, $Pb(C_2O_4)_2^{2-}$
12 would be insignificant, and therefore is not included in modeling solubilities of
13 $PbC_2O_4(cr)$ in NaCl media presented in this study.

14 The formation reaction for $PbC_2O_4(aq)$ can be expressed as:

15



17

18 The corresponding formation constant at infinite dilution would be,

19

20
$$\beta_1 = \frac{a_{PbC_2O_4(aq)}}{a_{Pb^{2+}} \times a_{C_2O_4^{2-}}} \quad (9)$$

21

1 where $a_{\text{PbC}_2\text{O}_4(\text{aq})}$, $a_{\text{Pb}^{2+}}$, and $a_{\text{C}_2\text{O}_4^{2-}}$ are activities for $\text{PbC}_2\text{O}_4(\text{aq})$, Pb^{2+} , and $\text{C}_2\text{O}_4^{2-}$,
2 respectively. Similarly, an apparent formation constant at a given ionic strength would
3 be expressed as,

4

$$5 \quad \beta_1^I = \frac{m_{\text{PbC}_2\text{O}_4(\text{aq})}}{m_{\text{Pb}^{2+}} \times m_{\text{C}_2\text{O}_4^{2-}}} \quad (10)$$

6

7 where $m_{\text{PbC}_2\text{O}_4(\text{aq})}$, $m_{\text{Pb}^{2+}}$, and $m_{\text{C}_2\text{O}_4^{2-}}$ are molalities for $\text{PbC}_2\text{O}_4(\text{aq})$, Pb^{2+} , and $\text{C}_2\text{O}_4^{2-}$,
8 respectively.

9 As there are apparent formation constants of $\text{PbC}_2\text{O}_4(\text{aq})$ as a function of
10 concentrations of KNO_3 in the literature (Table 3), these literature values are evaluated by
11 using the SIT model. Regarding Reaction (8), we have,

12

$$13 \quad \log \beta_I = \log \beta_1^I + 8D - \Delta\varepsilon \text{ (Eq. 8) } I_m \quad (11)$$

14

15 where $\Delta\varepsilon$ (Eq. 8) is given by the following equation for a KNO_3 medium,

16

$$17 \quad \Delta\varepsilon \text{ (Eq. 8) } = \varepsilon(\text{PbC}_2\text{O}_4(\text{aq}), \text{K}^+, \text{NO}_3^-) - \varepsilon(\text{Pb}^{2+}, \text{NO}_3^-) - \varepsilon(\text{K}^+, \text{C}_2\text{O}_4^{2-}) \quad (12)$$

18

19 In Figure 3, $\log \beta_1^I + 8D$ is plotted as a function of ionic strength in KNO_3
20 medium. The $\log \beta_I$ obtained in this plot is 5.40 ± 0.22 . In addition, based on $\Delta\varepsilon$ (Eq. 8)
21 $= 0.18 \pm 0.20$, $\varepsilon(\text{Pb}^{2+}, \text{NO}_3^-) = -0.20 \pm 0.12$ and $\varepsilon(\text{K}^+, \text{C}_2\text{O}_4^{2-}) = -0.25 \pm 0.19$,
22 $\varepsilon(\text{PbC}_2\text{O}_4(\text{aq}), \text{K}^+, \text{NO}_3^-)$ is derived as -0.27 ± 0.30 (Table 2).

1 Hedström et al. (1977) determined $\log \beta_1^I$ as 4.16 ± 0.02 in a 1 M NaClO₄

2 medium. In a NaClO₄ medium, $\Delta\epsilon$ (Eq. 8) has the following form,

3

4
$$\Delta\epsilon \text{ (Eq. 8)} = \epsilon(\text{PbC}_2\text{O}_4(\text{aq}), \text{Na}^+, \text{ClO}_4^-) - \epsilon(\text{Pb}^{2+}, \text{ClO}_4^-) - \epsilon(\text{Na}^+, \text{C}_2\text{O}_4^{2-}) \text{ (13)}$$

5

6 Using $\epsilon(\text{PbC}_2\text{O}_4(\text{aq}), \text{K}^+, \text{NO}_3^-) = -0.27 \pm 0.30$ obtained above as an analog to

7 $\epsilon(\text{PbC}_2\text{O}_4(\text{aq}), \text{Na}^+, \text{ClO}_4^-)$, and using $\epsilon(\text{Pb}^{2+}, \text{ClO}_4^-) = 0.15 \pm 0.02$ from Ciavatta (1980)

8 and $\epsilon(\text{Na}^+, \text{C}_2\text{O}_4^{2-}) = -0.02 \pm 0.05$ from Xiong (2009), $\log \beta_1^I$ is computed as 5.38 ± 0.31

9 according to Eq. (11). In the computation, the concentration of 1.0 M NaClO₄ on a molar

10 scale is converted to a molal scale based on the density equation for NaClO₄ (Söhnel and

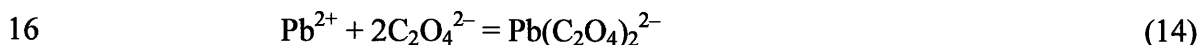
11 Novotný, 1985).

12 Based on the above values for $\log \beta_1^I$ obtained from both KNO₃ and NaClO₄

13 media, the average $\log \beta_1^I$ is calculated as 5.39 ± 0.38 (Table 2).

14 The formation reaction for $\text{Pb}(\text{C}_2\text{O}_4)_2^{2-}$ can be expressed as:

15



17

18 The corresponding formation constant at infinite dilution would be,

19

20
$$\beta_2 = \frac{a_{\text{Pb}(\text{C}_2\text{O}_4)_2^{2-}}}{a_{\text{Pb}^{2+}} \times (a_{\text{C}_2\text{O}_4^{2-}})^2} \quad (15)$$

21

1 where $a_{\text{Pb}(\text{C}_2\text{O}_4)_2^{2-}}$, $a_{\text{Pb}^{2+}}$, and $a_{\text{C}_2\text{O}_4^{2-}}$ are activities for $\text{Pb}(\text{C}_2\text{O}_4)_2^{2-}$, Pb^{2+} , and $\text{C}_2\text{O}_4^{2-}$,
2 respectively. Similarly, an apparent formation constant of $\text{Pb}(\text{C}_2\text{O}_4)_2^{2-}$ at a certain ionic
3 strength would be expressed as,

4

$$5 \quad \beta_2^I = \frac{m_{\text{Pb}(\text{C}_2\text{O}_4)_2^{2-}}}{m_{\text{Pb}^{2+}} \times (m_{\text{C}_2\text{O}_4^{2-}})^2} \quad (16)$$

6

7 where $m_{\text{Pb}(\text{C}_2\text{O}_4)_2^{2-}}$, $m_{\text{Pb}^{2+}}$, and $m_{\text{C}_2\text{O}_4^{2-}}$ are molalities for $\text{Pb}(\text{C}_2\text{O}_4)_2^{2-}$, Pb^{2+} , and $\text{C}_2\text{O}_4^{2-}$,
8 respectively.

9 As there are apparent formation constants of $\text{Pb}(\text{C}_2\text{O}_4)_2^{2-}$ as a function of
10 concentration of KNO_3 available in literature (Table 3), literature values are evaluated by
11 using the SIT model. Regarding Reaction (14), the following equation applies,

12

$$13 \quad \log \beta_2 = \log \beta_2^I + 8D - \Delta\varepsilon \text{ (Eq. 14) } I_m \quad (17)$$

14

15 where $\Delta\varepsilon$ (Eq. 14) is given by the following equation for a KNO_3 medium,

16

$$17 \quad \Delta\varepsilon \text{ (Eq. 14)} = \varepsilon(\text{K}^+, \text{Pb}(\text{C}_2\text{O}_4)_2^{2-}) - \varepsilon(\text{Pb}^{2+}, \text{NO}_3^-) - 2 \times \varepsilon(\text{K}^+, \text{C}_2\text{O}_4^{2-}) \quad (18)$$

18

19 In Figure 4, $\log \beta_2^I + 8D$ is plotted as a function of ionic strength in KNO_3 media.

20 The $\log \beta_2$ obtained from this plot is 7.35 ± 0.21 . In addition, based on $\Delta\varepsilon$ (Eq. 14) =

1 0.18 ± 0.20 , $\varepsilon(\text{Pb}^{2+}, \text{NO}_3^-) = -0.20 \pm 0.12$ and $\varepsilon(\text{K}^+, \text{C}_2\text{O}_4^{2-}) = -0.25 \pm 0.19$, $\varepsilon(\text{K}^+$,
2 $\text{Pb}(\text{C}_2\text{O}_4)_2^{2-})$ is derived as -0.52 ± 0.30 (Table 2).

3 Hedström et al. (1977) determined $\log \beta_2^I$ as 6.33 ± 0.02 in 1.0 M NaClO_4 media.

4 In NaClO_4 media, $\Delta\varepsilon$ (Eq. 14) has the following form,

5

$$6 \quad \Delta\varepsilon \text{ (Eq. 14)} = \varepsilon(\text{Na}^+, \text{Pb}(\text{C}_2\text{O}_4)_2^{2-}) - \varepsilon(\text{Pb}^{2+}, \text{ClO}_4^-) - 2 \times \varepsilon(\text{Na}^+, \text{C}_2\text{O}_4^{2-}) \quad (19)$$

7

8 Using $\varepsilon(\text{K}^+, \text{Pb}(\text{C}_2\text{O}_4)_2^{2-}) = -0.52 \pm 0.30$ obtained above as an analog to

9 $\varepsilon(\text{Na}^+, \text{Pb}(\text{C}_2\text{O}_4)_2^{2-})$, and using $\varepsilon(\text{Pb}^{2+}, \text{ClO}_4^-) = 0.15 \pm 0.02$ from Ciavatta (1980) and

10 $\varepsilon(\text{Na}^+, \text{C}_2\text{O}_4^{2-}) = -0.02 \pm 0.05$ from Xiong (2009), $\log \beta_2$ is computed as 7.31 ± 0.31

11 according to Eq. (17). In the computation, the concentration of 1.0 M NaClO_4 on a molar

12 scale is converted to a molal scale based on the density equation for NaClO_4 (Söhnel and

13 Novotný, 1985).

14 Based on the above values for $\log \beta_2$ obtained from both KNO_3 and NaClO_4

15 media, the average $\log \beta_1$ is calculated as 7.33 ± 0.37 (Table 2).

16 In comparison, the above $\log \beta_1$ and $\log \beta_2$ evaluated by using the SIT model are

17 significantly, and systematically, higher than respective values calculated by Klatt (1970)

18 using the Davies equation (Table 3). The difference is about 0.5 logarithmic units. The

19 $\log \beta_1$ evaluated from solubility of PbC_2O_4 (cr) in NaCl presented in this study is slightly

20 higher than that evaluated from the literature data by using the SIT model, but is within

21 the quoted uncertainties. The $\log \beta_2$ (8.05 ± 0.07) evaluated from solubilities of

22 PbC_2O_4 (cr) in $\text{K}_2\text{C}_2\text{O}_4$ media from Kolthoff et al. (1942) by this study is close to the

1 value of 7.80 ± 0.36 computed from a single value of $\log \beta_2^I$ in NaClO_4 using the SIT
2 model, but is significantly higher than the value of 7.35 ± 0.36 evaluated from $\log \beta_2^I$'s
3 in a KNO_3 medium by using the SIT model. From Figure 1, we can see that the $\log \beta_2$ of
4 8.05 ± 0.07 along with $\log \beta_1 = 5.85 \pm 0.10$ and $\log K_{\text{sp}} = -11.13 \pm 0.10$ reproduces
5 solubility data of Kolthoff et al. (1942) well.

6

7 *The Importance of $\text{PbC}_2\text{O}_4(\text{cr})$ and Soluble Lead Oxalate Complexes in Low*
8 *Temperature Environments*

9 As detailed in the above sections, lead oxalate has low solubility, and soluble lead
10 oxalate complexes are relatively strong. These will have important implications to
11 solubility of lead and other soluble oxalate complexes in low temperature environments.
12 For instance, in environments of geological repositories, Pb^{2+} will strongly compete with
13 actinide ions for soluble oxalate, lowering total solubilities of actinides. This is because
14 the $\log \beta_1$'s for AmC_2O_4^+ and $\text{NpOC}_2\text{O}_4^-$ are 6.16 and 4.24, respectively (Xiong, 2005;
15 Xiong et al., 2010b; also see data0.fmt in Wolery et al., 2010). In comparison, $\log \beta_1$ and
16 $\log \beta_2$ for $\text{PbC}_2\text{O}_4(\text{aq})$ and $\text{Pb}(\text{C}_2\text{O}_4)_2^{2-}$ are 5.85 and 8.05, respectively, as described
17 above.

18 In addition, in the INTRODUCTION section, it is summarized that pyromorphite
19 would be converted to $\text{PbC}_2\text{O}_4(\text{cr})$ in environments where there are microbial activities.
20 Therefore, $\text{PbC}_2\text{O}_4(\text{cr})$ or other Pb-containing phase(s) would become the source-term, or
21 solubility-controlling phase for lead instead of pyromorphite. To quantitatively
22 demonstrate this scenario, we perform solubility calculations in a model soil solution.
23 The model soil solution we employed is the one used in Xiong (2009), which was

1 modified from the original recipe developed by Wood (2000). In our solubility
2 calculations, it is assumed that oxalate concentrations are controlled by the solubility of
3 whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), which along with weddellite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) is commonly
4 observed in soils (e.g., Murnut and Pape, 1971; Graustein and Cromack, 1977). As the
5 model soil solution has a low ionic strength, we use the data0.suv database (Wolery,
6 1992) for solubility calculations. Another consideration of using the data0.suv database
7 is that this database contains all elements in the model soil solution. For our solubility
8 calculations, the data0.suv database incorporates above constants determined in this
9 study, and the $\log K_{sp}$'s of PbClOH (cr) and litharge (PbO) from Powell et al. (2009), and
10 of whewellite from the data0.fmt database (Wolery et al., 2010; Xiong, 2011). In
11 addition, the $\log K_{sp}$ for the pure-end member of pyromorphite from Flis et al. (2011) is
12 also incorporated into the data0.suv database.

13 In Figure 5, solubilities of anglesite, cerussite, litharge, PbClOH (cr), lead oxalate,
14 and pyromorphite, as a function of pH in the model soil solution, are displayed. The
15 solubilities of pyromorphite are presented as a reference. From Figure 5, it is obvious
16 that litharge and PbClOH (cr) are unstable in the pH range lower than pH 7.5. In the pH
17 range where they are stable, they have relatively higher solubilities. Therefore, litharge
18 or PbClOH (cr) would not be the solubility-controlling phase for lead in soil
19 environments. Although anglesite is stable over the entire pH range in Figure 5, it would
20 not be the solubility-controlling phase for lead because of its relatively higher solubilities.
21 Regarding cerussite, it is unstable below pH 5, and it has higher solubilities than lead
22 oxalate in the pH range from 5 to ~7.5. Cerussite has lower solubilities than lead oxalate
23 in alkaline pH. Regarding lead oxalate, it is stable over the entire pH range, and it even

1 has lower solubilities than pyromorphite in the pH range below 6. Therefore, we can
2 conclude that when pyromorphite is converted to lead oxalate by microbial activities,
3 lead oxalate is expected to be a solubility-controlling phase for lead in the pH range from
4 acidic to mildly basic. If crystallization of cerussite is kinetically favored in soil
5 environments, cerussite would be a solubility-controlling phase for lead in alkaline pH
6 range.

7 It is of interest to note that in the study of Debela et al. (2010) on solubility of
8 pyromorphite in oxalic acid mimicking its concentrations in soil solutions in a 0.01 M
9 NaNO₃ background solution, the authors found out that lead concentrations range from
10 8.9×10^{-6} M (-5.05 in logarithmic units) to 1.8×10^{-5} M (-4.74 in logarithmic units) in
11 the acidic pH range. In comparison with the lead concentrations controlled by lead
12 oxalate (Figure 5), the above lead concentrations in oxalic acid characteristic of soil
13 solutions are higher. Therefore, lead oxalate evidently should be a solubility-controlling
14 phase for lead in the acidic pH range even in the presence of pyromorphite.

15

16 SUMMARY

17 In this study, $\log K_{sp}$ for lead oxalate, $\log \beta_1$ for PbC₂O₄(aq), and $\log \beta_2$ for
18 Pb(C₂O₄)₂²⁻ are evaluated from experimental data to high ionic strengths. Relevant Pitzer
19 interaction parameters and the Brønsted-Guggenheim-Scatchard SIT coefficients
20 consistent with the above $\log K_{sp}$, $\log \beta_1$, and $\log \beta_2$ are also obtained. These constants
21 and parameters would enable us to model the solubility of PbC₂O₄(cr), and the
22 interactions of PbC₂O₄(aq) and Pb(C₂O₄)₂²⁻ with the media including NaCl, KNO₃ and
23 K₂C₂O₄ to high ionic strengths.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23

ACKNOWLEDGEMENTS

Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000. This research is funded by WIPP programs administered by the Office of Environmental Management (EM) of the U.S Department of Energy. We are grateful to Shelly Nielsen, Terry MacDonald, Tana Saul, Diana Goulding, Brittany Hoard, Cassandra Marrs, Danelle Morrill, Mathew Stroble, and Kira Vicent, for their laboratory assistance.

REFERENCES

Adeyemi, A.O., and Gadd, G.M., 2005. Fungal degradation of calcium-, lead- and silicon-bearing minerals. *BioMetals* **18**, 269–281.

Borkowski, M., Choppin, G.R., Moore, R., 2000. Thermodynamic modeling of metal-ligand interactions in high ionic strength NaCl solutions: The Co^{2+} -oxalate system. *Radiochimica Acta* **88**, 599–602.

Brush, L.H., and Xiong, Y.-L., 2009. Calculation of organic-ligand concentrations for the WIPP CRA-2009 PABC. Analysis Report, June 16, 2009. Carlsbad, NM: Sandia National Laboratories, ERMS 551481.

- 1 Ciavatta, L., 1980. The specific interaction theory in evaluating ionic equilibria. *Annali*
2 *di Chimica* **70**, 551–567.
- 3 Debela, F., Arocena, J.M., Thring, R.W., Whitcombe, T., 2010. Organic acid-induced
4 release of lead from pyromorphite and its relevance to reclamation of Pb-
5 contaminated soils. *Chemosphere* **80**, 450–456.
- 6 Diez-Caballero, R.J.B., Valentin, J.F.A., Garcia, A.A., Almudi, R.P., and Batanero, P.S., 1985.
7 Polarographic determination of the stability constants of binary and ternary
8 lead(II) complexes and different organic ligands. *Journal of Electroanalytical*
9 *Chemistry* **196**, 43–51.
- 10 Felmy, A.R., Onishi, L.M., Foster, N.S., Rustad, J.R., Rai, D., and Mason, M.J., 2000.
11 An aqueous thermodynamic model for the Pb^{2+} – Na^+ – K^+ – Ca^{2+} – Mg^{2+} – H^+ – Cl^- –
12 SO_4^{2-} – H_2O system to high concentration: Application to WIPP brines.
13 *Geochimica et Cosmochimica Acta* **64**, 3615–3628.
- 14 Flis, J., Manecki, J., and Bajda, T., 2011. Solubility of pyromorphite $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ –
15 mimetite $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$ solid solution series. *Geochimica et Cosmochimica Acta*
16 **75**, 1858–1868.
- 17 Fomina, M.A., Alexander, I.J., Hillier, S., and Gadd, G.M., 2004. Zinc phosphate and
18 pyromorphite solubilization by soil plant-symbiotic fungi. *Geomicrobiology*
19 *Journal* **21**, 351–366.
- 20 Fomina, M.A., Alexander, I.J., Colpaert, J.V., and Gadd, G.M., 2005. Solubilization of
21 toxic metal minerals and metal tolerance of mycorrhizal fungi. *Soil Biology and*
22 *Biochemistry* **37**, 851–866.

- 1 Fomina, M., Charnock, J., Bowen, A.D., Gadd, G.M., 2007. X-ray absorption
2 spectroscopy (XAS) of toxic metal mineral transformations by fungi.
3 *Environmental Microbiology* **9**, 308–321.
- 4 Gadd, G.M., 2000. Bioremedial potential of microbial mechanisms of metal mobilization
5 and immobilization. *Current Opinion in Biotechnology* **11**, 271–279.
- 6 Graustein, W., and Cromack, K. Jr., 1977. Calcium oxalate: occurrence in soils and
7 effect on nutrient and geochemical cycles. *Science* **198**, 1252–1254.
- 8 Grenthe, I., Wanner, H., Östhols, E., 2000. TDB-2: Guidelines for the extrapolation to
9 zero ionic strength. OECD Nuclear Energy Agency, Data Bank, Report, 34 pp.
- 10 Hedström, H., Olin, Å., Svanström, P., and Åslin, E., 1977. The complex formation
11 between Pb^{2+} and the oxalate and hydrogen oxalate ions: A solubility study.
12 *Journal of Inorganic and Nuclear Chemistry* **39**, 1191–1194.
- 13 Helgeson, H.C., and Kirkham, D.H., 1974. Theoretical prediction of the thermodynamic
14 behavior of aqueous electrolytes at high pressures and temperatures. II. Debye–
15 Hückel parameters for activity coefficients and relative partial molal properties.
16 *American Journal of Sciences* **274**, 1199–1261.
- 17 Jain, D.S., Kumar, A., and Gaur, J.N., 1968. Composition and stability constants of
18 oxalate complexes of lead by a polarographic method. *Electroanalytical*
19 *Chemistry and Interfacial Electrochemistry* **17**, 201–205.
- 20 Klatt, L.N., 1970. Complex formation in lead oxalate solutions. *Analytical Chemistry*
21 **42**, 1837–1839.
- 22 Kolthoff, I.M., Perlich, R.W., and Weiblen, D., 1942. The solubility of lead sulfate and
23 of lead oxalate in various media. *Journal of Physical Chemistry* **46**, 561–570.

- 1 Krishnamurty, K.V., and Harris, G.M., 1961. The chemistry of the metal oxalato
2 complexes. *Chemical Reviews* **61**, 213–246.
- 3 Kubacky-Beard, U., Casey, W.H., Castles, J.J., and Rock, P.A., 1996. Standard Gibbs
4 energies of formation of $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (s), $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ (s), $\text{Hg}_2\text{C}_2\text{O}_4$ (s), and
5 PbC_2O_4 (s) at 298 K and 1 bar. *Geochimica et Cosmochimica Acta* **60**, 1283–
6 1289.
- 7 Luo, Y.-X., and Millero, F.J., 2007. Stability constants for the formation of lead chloride
8 complexes as a function of temperature and ionic strength. *Geochimica et*
9 *Cosmochimica Acta* **71**, 326–334.
- 10 Millero, F.J., and Byrne, R.H., 1984. Use of Pitzer's equation to determine the media
11 effect on the formation of lead chloro complexes. *Geochimica et Cosmochimica*
12 *Acta* **48**, 1145–1150.
- 13 Murmut, A., Pape, Th., 1971. Micromorphology of two soils from Turkey, with special
14 reference to *in situ* formation of clay cutans. *Geoderma* **5**, 271–281.
- 15 Nemer, M., Xiong, Y.-L., Ismail, A.E., and Jang, J.-H., 2011. Solubility of $\text{Fe}_2(\text{OH})_3\text{Cl}$
16 (pure-iron end-member of hibbingite) in NaCl and Na_2SO_4 brines. *Chemical*
17 *Geology* **280**, 26–32.
- 18 Nordstrom, D.K., and Munoz, J.L., 1986. *Geochemical Thermodynamics*. Blackwell
19 Scientific Publications, Boston, MA, 477 pp.
- 20 Nyholm, L., and Wikmark, G., 1989. Precise polarographic determination of the stability
21 constants of cadmium and lead with oxalate and sulfate. *Analytica Chimica Acta*
22 **223**, 429–440.

- 1 Perrin, D.D., 1979. Stability Constants of Metal-Ion Complexes, Part B: Organic
2 Ligands, IUPAC Chemical Data Series, No. 22, Pergamon, New York.
- 3 Popielak, R.S., Beauheim, R.L., Black, S.R., Coons, W.E., Ellingson, C.T., and Olsen,
4 R.L., 1983. *Brine Reservoirs in the Castile Formation, Waste Isolation Pilot
5 Plant Project, Southeastern New Mexico*. TME 3153. Carlsbad, NM: U.S.
6 Department of Energy WIPP Project Office.
- 7 Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Luez, A.-K., Sjöberg, S.,
8 and Wanner, H., 2009. Chemical speciation of environmentally significant metals
9 with inorganic ligands. Part 3: The $Pb^{2+} + OH^-$, Cl^- , CO_3^{2-} , SO_4^{2-} , and PO_4^{3-}
10 systems (IUPAC Technical Report). *Pure and Applied Chemistry* **81**, 2425-2476.
- 11 Sayer, J.A., Cotter-Howells, J.D., Watson, C., Hillier, S., Gadd, G.M., 1999. Lead
12 mineral transformation by fungi. *Current Biology* **9**, 691-694.
- 13 Söhnel, O. and Novotný, P., 1985. Densities of aqueous solutions of inorganic
14 substances. Elsevier, New York, 335 p.
- 15 U.S. DOE, 2004. *Title 40 CFR Part 191 Compliance Recertification Application for the
16 Waste Isolation Pilot Plant, Vol. 1-8*. DOE/WIPP 2004-3231. Carlsbad, NM:
17 U.S. DOE Carlsbad Field Office.
- 18 Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M.,
19 Churney, K.L., Buttall, R.L., 1982. The NBS tables of chemical thermodynamic
20 properties. Selected values for inorganic and C1 and C2 organic substances in SI
21 units. *Journal of Physical Chemistry Reference Data* **11** (Suppl.2), 392.

- 1 Wolery, T.J., 1992. EQ3/6, A Software Package for Geochemical Modeling of Aqueous
2 Systems: Package Overview and Installation Guide (Version 7.0), UCRL-MA-
3 110662-PT-I (Lawrence Livermore National Laboratory: Livermore, CA).
- 4 Wolery, T.W., Xiong, Y.-L., and Long, J., 2010. Verification and Validation
5 Plan/Validation Document for EQ3/6 Version 8.0a for Actinide Chemistry,
6 Document Version 8.10. Carlsbad, NM: Sandia National laboratories. ERMS
7 550239.
- 8 Wood, S.A., 2000. Organic matter: Supergene Enrichment and Dispersion, in *Ore*
9 *Genesis and Exploration: The Roles of organic matter. Reviews in Economic*
10 *Geology, Vol. 9* (Eds T. H. Giordano, R. M. Kettler, S. A. Wood), pp. 157–192
11 (Society of Economic Geologist: Littleton, CO).
- 12 Xiong, Y.-L., 2005. Release of FMT_050405.CHEMDAT. Carlsbad, NM: Sandia
13 National Laboratories, ERMS 539304.
- 14 Xiong, Y.-L., 2008. Thermodynamic properties of brucite determined by solubility
15 studies and their significance to nuclear waste isolation. *Aquatic Geochemistry*
16 *14*, 223–238.
- 17 Xiong, Y.-L., 2009. The aqueous geochemistry of thallium: speciation and solubility of
18 thallium in low temperature systems. *Environmental Chemistry* *6*, 441–451.
- 19 Xiong, Y.-L., 2011. WIPP Verification and Validation Plan/Validation Document for
20 EQ3/6 Version 8.0a for Actinide Chemistry, Revision 1, Document Version 8.20.
21 Supersedes ERMS 550239. Carlsbad, NM. Sandia National Laboratories.
22 ERMS 555358.

- 1 Xiong, Y.-L., and Lord, A.S., 2008. Experimental investigations of the reaction path in
2 the MgO–H₂O–CO₂ system in solutions with various ionic strengths, and their
3 applications to nuclear waste isolation. *Applied Geochemistry* **23**, 1634–1659.
4 DOI:10.1016/j.apgeochem.2007.12.035.
- 5 Xiong, Y.-L., Deng, H.-R., Nemer, M., and Johnsen, S., 2010a. Experimental
6 determination of the solubility constant for magnesium chloride hydroxide
7 hydrate (Mg₃Cl(OH)₅·4H₂O), phase 5) at room temperature, and its importance to
8 nuclear waste isolation in geological repositories in salt formations. *Geochimica
9 et Cosmochimica Acta* **74**, 4605–46011.
- 10 Xiong, Y.-L., Nowak, J., Brush, L.H., Ismail, A.E., Long, J.J., 2010b. Establishment of
11 uncertainty ranges and probability distributions of actinide solubilities for
12 performance assessment in the Waste Isolation Pilot Plant. *Materials Res. Soc.
13 Symp. Proc.*, **1265**, 15–20.
14

1 Table 1. Experimental results concerning solubility of $\text{PbC}_2\text{O}_4(\text{cr})$ in NaCl medium
 2

Experimental Number	Supporting Medium, NaCl, molal	Experimental Time, day	$\text{pH}_{\text{Ob}}^{\text{A}}$	Solubility Expressed As Total Pb On Molal Scale ($m_{\Sigma\text{Pb}}$)	Concentration of Oxalate on Molal Scale
PbOx-0.01-1	0.010	109	6.40	2.52×10^{-5}	BDL ^C
		551	6.30	1.37×10^{-5}	BDL
		780	6.01	2.02×10^{-5}	BDL
		831	6.30	2.23×10^{-5}	BDL
		1062	6.46	3.45×10^{-5}	BDL
PbOx-0.01-2	0.010	109	6.51	2.38×10^{-5}	BDL
		551	6.30	1.61×10^{-5}	BDL
		780	6.00	2.22×10^{-5}	BDL
		831	6.54	2.66×10^{-5}	BDL
		1062	6.37	2.81×10^{-5}	BDL
PbOx-0.1-1	0.10	109	6.03	3.84×10^{-5}	BDL
		551	6.06	2.69×10^{-5}	BDL
		780	5.77	3.04×10^{-5}	BDL
		831	6.22	3.19×10^{-5}	1.43×10^{-5}
		1062	6.24	3.41×10^{-5}	BDL
PbOx-0.1-2	0.10	109	5.88	3.84×10^{-5}	BDL
		551	5.49	2.80×10^{-5}	BDL
		780	5.21	3.17×10^{-5}	BDL
		831	5.43	3.36×10^{-5}	1.40×10^{-5}
		1062	5.31	3.53×10^{-5}	BDL
PbOx-1.0-1	1.0	109	6.55	$1.37 \pm 0.02 \times 10^{-4\text{B}}$	1.08×10^{-4}
		551	6.80	1.14×10^{-4}	3.30×10^{-4}
		780	6.88	9.96×10^{-5}	3.29×10^{-4}
		831	6.88	1.08×10^{-4}	3.18×10^{-4}
		1062	6.77	1.48×10^{-4}	2.55×10^{-4}
PbOx-1.0-2	1.0	109	6.53	$1.40 \pm 0.01 \times 10^{-4\text{B}}$	1.34×10^{-4}
		551	6.81	1.14×10^{-4}	3.74×10^{-4}
		780	6.93	1.04×10^{-4}	5.43×10^{-5}
		831	6.73	1.11×10^{-4}	3.27×10^{-4}
		1062	6.81	1.39×10^{-4}	2.44×10^{-4}
PbOx-2.0-1	2.1	109	6.11	$3.05 \pm 0.01 \times 10^{-4\text{B}}$	-----
		551	5.86	2.01×10^{-4}	-----
		780	5.70	2.68×10^{-4}	-----
		831	5.66	2.71×10^{-4}	-----
		1062	5.63	3.17×10^{-4}	-----
PbOx-2.0-2	2.1	109	6.19	$3.72 \pm 0.04 \times 10^{-4\text{B}}$	-----
		551	6.10	1.95×10^{-4}	-----
		780	6.38	2.73×10^{-4}	-----

		831	6.00	2.72×10^{-4}	-----
		1062	6.19	3.19×10^{-4}	-----
PbOx-3.0-1	3.2	109	6.14	$7.23 \pm 0.17 \times 10^{-4}$ ^B	-----
		551	5.85	6.22×10^{-4}	-----
		780	5.98	6.78×10^{-4}	-----
		831	5.63	6.73×10^{-4}	-----
		1062	5.71	7.69×10^{-4}	-----
PbOx-3.0-2	3.2	109	6.23	$7.34 \pm 0.10 \times 10^{-4}$ ^B	-----
		551	6.07	6.06×10^{-4}	-----
		780	6.30	6.97×10^{-4}	-----
		831	5.85	6.73×10^{-4}	-----
		1062	6.13	7.76×10^{-4}	-----
PbOx-4.0-1	4.4	109	6.56	$1.65 \pm 0.00 \times 10^{-3}$ ^B	-----
		551	6.38	1.57×10^{-3}	-----
		780	6.58	1.62×10^{-3}	-----
		831	6.12	1.62×10^{-3}	-----
		1062	6.37	1.78×10^{-3}	-----
PbOx-4.0-2	4.4	109	6.62	$1.67 \pm 0.01 \times 10^{-3}$ ^B	-----
		551	6.37	1.58×10^{-3}	-----
		780	6.46	1.68×10^{-3}	-----
		831	6.44	1.64×10^{-3}	-----
		1062	6.38	1.84×10^{-3}	-----
PbOx-5.0-1	5.0	109	7.12	$3.07 \pm 0.04 \times 10^{-3}$ ^B	-----
		551	6.88	3.03×10^{-3}	-----
		780	7.05	3.17×10^{-3}	-----
		831	6.72	3.06×10^{-3}	-----
		1062	6.87	3.52×10^{-3}	-----
PbOx-5.0-2	5.0	109	7.15	$3.03 \pm 0.02 \times 10^{-3}$ ^B	-----
		551	6.95	3.05×10^{-3}	-----
		780	7.27	3.18×10^{-3}	-----
		831	7.09	3.10×10^{-3}	-----
		1062	6.95	3.29×10^{-3}	-----

1 ^A pH readings obtained by using a pH electrode, and they can be converted to hydrogen
2 ion concentrations by applying correction factors (see text for detail).

3 ^B Replicate analyses, and uncertainty represents two standard deviations (2σ).

4 ^C Below detection limit.

5 Experimental data contained in this table are from the scientific notebooks WIPP-
6 SOLUBILITY-3 and WIPP- SOLUBILITY-12, and associated binders.

7
8
9

1
2
3
4
5

Table 2. Equilibrium constants at infinite dilution, 25°C and 1 bar, Pitzer interaction parameters, and Brønsted-Guggenheim-Scatchard SIT interaction coefficients in Na⁺—K⁺—Pb²⁺—Cl⁻—NO₃⁻—ClO₄⁻—C₂O₄²⁻ system

Reactions	log K_{sp} or log β_n	Reference and Remarks
$\text{PbC}_2\text{O}_4(\text{cr}) = \text{Pb}^{2+} + \text{C}_2\text{O}_4^{2-}$	$-10.50 \pm 0.29 (2\sigma)^{[1]}$	This study, evaluated from literature data, the SIT model
	$-11.13 \pm 0.10 (2\sigma)$	This study, based on solubility of $\text{PbC}_2\text{O}_4(\text{cr})$ in NaCl medium presented in the present work, Pitzer model
$\text{Pb}^{2+} + \text{C}_2\text{O}_4^{2-} = \text{PbC}_2\text{O}_4(\text{aq})$	$5.39 \pm 0.38 (2\sigma)^{[2]}$	This study, evaluated from literature data, the SIT model
	$5.85 \pm 0.10 (2\sigma)$	This study, based on solubility of $\text{PbC}_2\text{O}_4(\text{cr})$ in NaCl medium presented in the present work, Pitzer model
$\text{Pb}^{2+} + 2\text{C}_2\text{O}_4^{2-} = \text{Pb}(\text{C}_2\text{O}_4)_2^{2-}$	$7.33 \pm 0.37 (2\sigma)^{[3]}$	This study, evaluated from literature data, the SIT model
	$8.05 \pm 0.07 (2\sigma)$	This study, evaluated from solubilities of $\text{PbC}_2\text{O}_4(\text{cr})$ in $\text{K}_2\text{C}_2\text{O}_4$ medium from Kolthoff et al. (1942), Pitzer model
$\text{Pb}^{2+} + \text{Cl}^- = \text{PbCl}^+$	1.48	Millero and Byrne (1984), evaluated by using Pitzer model; uncertainty not given
	$1.50 \pm 0.03 (2\sigma)$	Powell et al. (2009), evaluated by using the SIT model
$\text{Pb}^{2+} + 2\text{Cl}^- = \text{PbCl}_2(\text{aq})$	2.03	Millero and Byrne (1984), evaluated by using Pitzer model; uncertainty not given
	$2.10 \pm 0.05 (2\sigma)$	Powell et al. (2009), evaluated by using the SIT model
$\text{Pb}^{2+} + 3\text{Cl}^- = \text{PbCl}_3^-$	1.86	Millero and Byrne (1984), evaluated by using Pitzer model; uncertainty not given
	$2.00 \pm 0.10 (2\sigma)$	Powell et al. (2009),

					evaluated by using the SIT model
Pitzer Binary Interaction Parameters					
Species <i>i</i>	Species <i>j</i>	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	
Pb ²⁺	Cl ⁻	0.26	1.64	0.088	Millero and Byrne (1984)
PbCl ⁺	Cl ⁻	0.15	0	0	Millero and Byrne (1984)
Na ⁺	PbCl ₃ ⁻	-0.0605	0	0.091	This study
K ⁺	Pb(C ₂ O ₄) ₂ ²⁻	0	-1.86	0.198	This study
Na ⁺	Pb(C ₂ O ₄) ₂ ²⁻	0	-1.86	0.198	This study, in analog to K ⁺ —Pb(C ₂ O ₄) ₂ ²⁻
Pitzer Mixing Interaction Parameters and Interaction Parameters Involving Neutral Species					
Species <i>i</i>	Species <i>j</i>	Species <i>k</i>	λ_{ij} or θ_{ij}	ζ_{ijk}	
Cl ⁻	PbCl ₂ (aq)		-0.14		This study
Na ⁺	PbCl ₂ (aq)		-0.11		Felmy et al. (2000)
Na ⁺	Pb ²⁺		0.10		Felmy et al. (2000)
Na ⁺	PbCl ₂ (aq)	Cl ⁻		0	This study
Na ⁺	PbC ₂ O ₄ (aq)	Cl ⁻	0	0	This study
Brønsted-Guggenheim-Scatchard SIT interaction Coefficients					
Species <i>i</i>	Species <i>j</i>	Species <i>k</i>	ε_{ij}	ε_{ijk} (for neutral species)	
Pb ²⁺	ClO ₄ ⁻		0.15 ± 0.02		Ciavatta (1980)
Pb ²⁺	NO ₃ ⁻		-0.20 ± 0.12		Ciavatta (1980)
Na ⁺	C ₂ O ₄ ²⁻		-0.02 ± 0.05		Xiong (2009)
K ⁺	C ₂ O ₄ ²⁻		-0.25 ± 0.19		This study
K ⁺	NO ₃ ⁻	PbC ₂ O ₄ (aq)		-0.27 ± 0.30	This study
K ⁺	Pb(C ₂ O ₄) ₂ ²⁻		-0.52 ± 0.30		This study

1
2
3
4
5
6
7
8
9
10
11

[1] Average value of the solubility product constant ($\log K_{sp}$) evaluated from KNO₃ and NaClO₄ media, and the $\log K_{sp}$ determined by using the electrochemical cell method. See text for details.

[2] Average value of $\log \beta_1$ evaluated from KNO₃ and NaClO₄ media. See text for details.

[3] Average value of $\log \beta_2$ evaluated from KNO₃ and NaClO₄ media. See text for details.

1

2 Table 3. Literature values for formation constants of aqueous lead oxalate complexes

Ionic strength	T °C	$\log \beta'_1$	$\log \beta'_2$	Experimental Method	Reference
1.5 M KNO ₃	30	3.3	5.0	Polarographic	Jain et al., 1968
0 ^A	25	4.91	6.76	Solubility	Klatt, 1970
0.15 KNO ₃	25	4.39	6.21	Solubility	Recalculated by Hedström et al. (1977) based on the original data of Klatt (1970).
0.30 KNO ₃	25	4.16	6.04	Solubility	Recalculated by Hedström et al. (1977) based on the original data of Klatt (1970).
0.50 KNO ₃	25	4.02	5.83	Solubility	Recalculated by Hedström et al. (1977) based on the original data of Klatt (1970).
1.0 KNO ₃	25	3.53	5.73	Solubility	Recalculated by Hedström et al. (1977) based on the original data of Klatt (1970).
1.5 KNO ₃	25	3.58	5.34	Solubility	Recalculated by Hedström et al. (1977) based on the original data of Klatt (1970).
1.0 NaClO ₄	25	4.16	6.33	Solubility	Hedström et al. (1977)
1 M KNO ₃	25	3.33	5.53	Polarographic	Perrin, 1979
1 M KNO ₃	25	3.6	5.56	Polarographic	Diez-Caballero et al., 1985
1 M KNO ₃	25	3.4	5.60	Polarographic	Nyholm and Wikmark, 1989

^A extrapolated to infinite dilution by using the Davies equation by the original author.

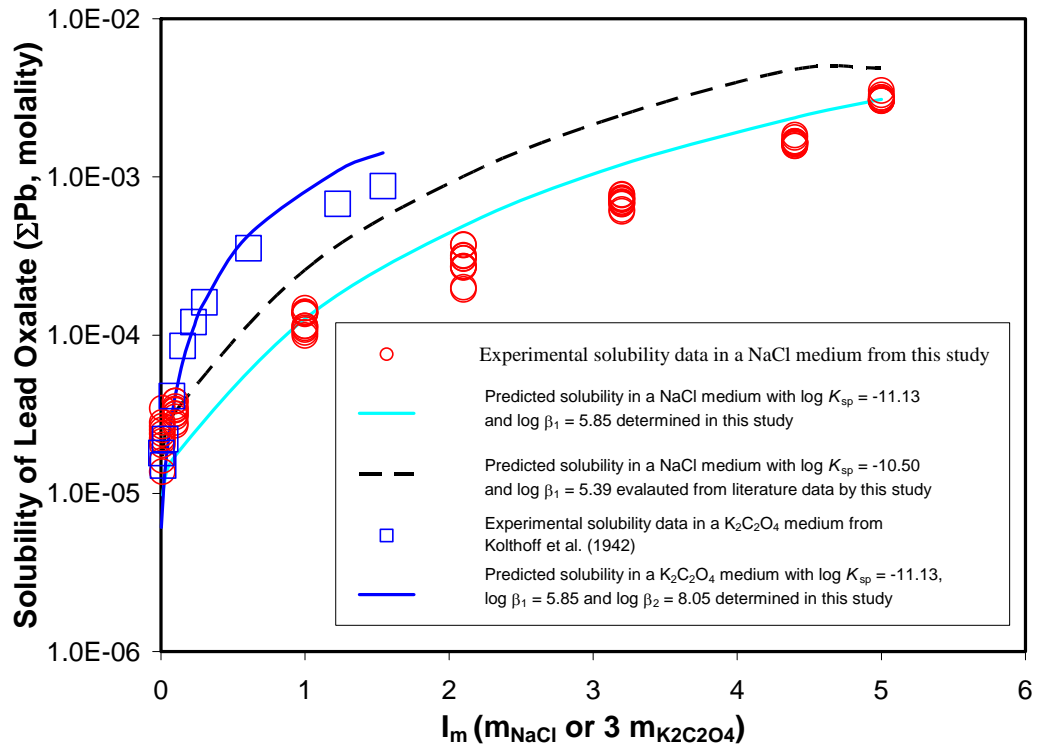
3

4

5

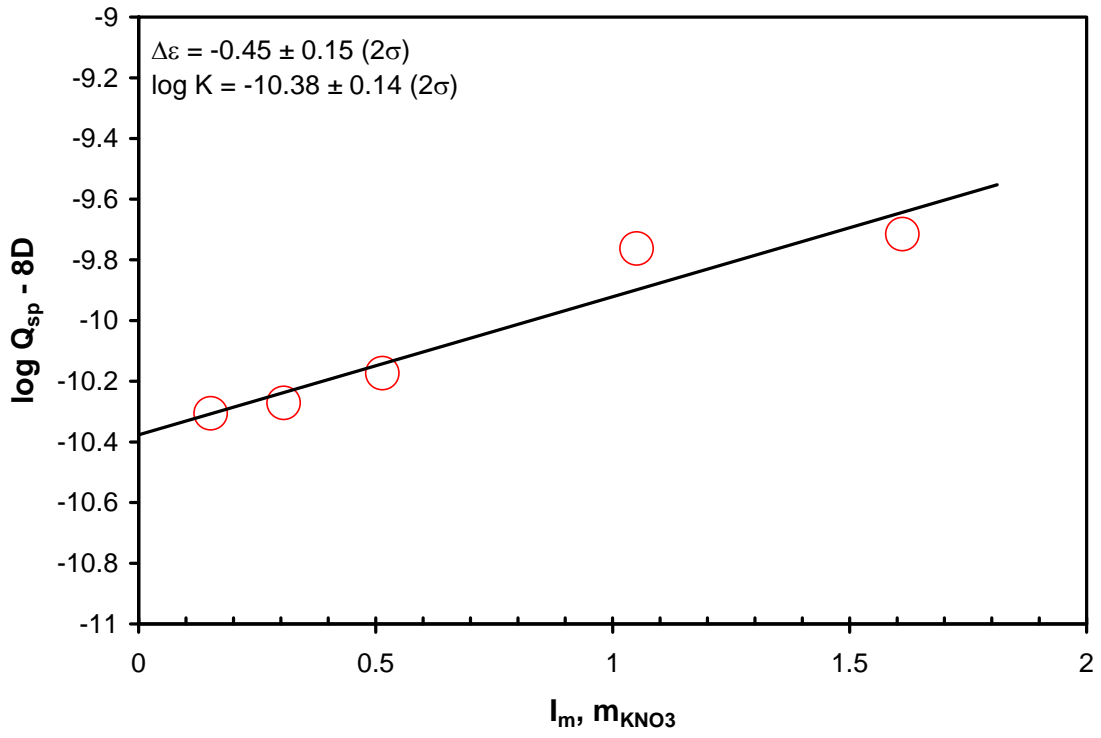
6

7

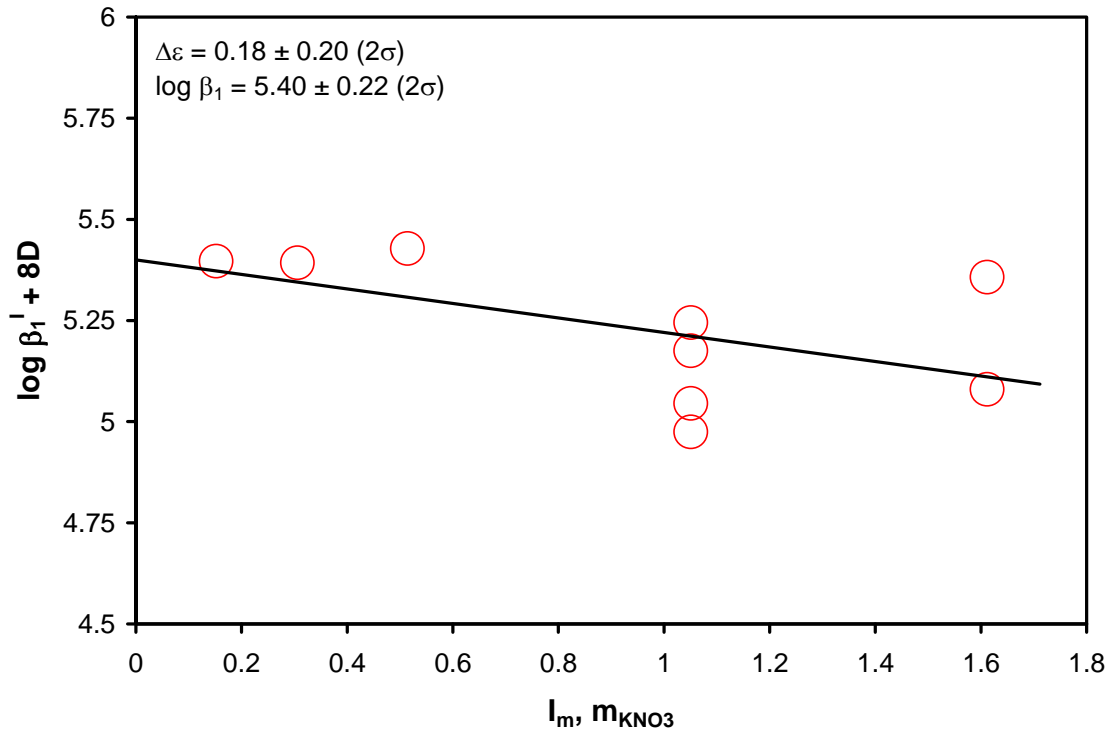


1
2
3
4
5

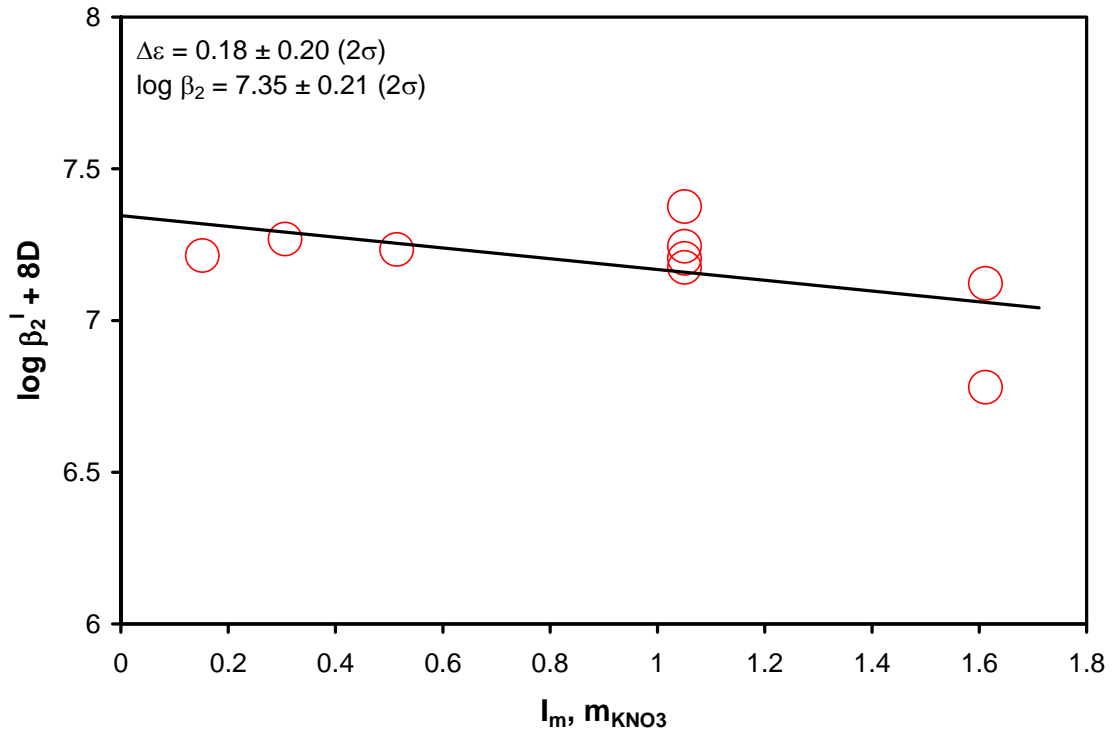
Figure 1



1
2 Figure 2
3
4
5



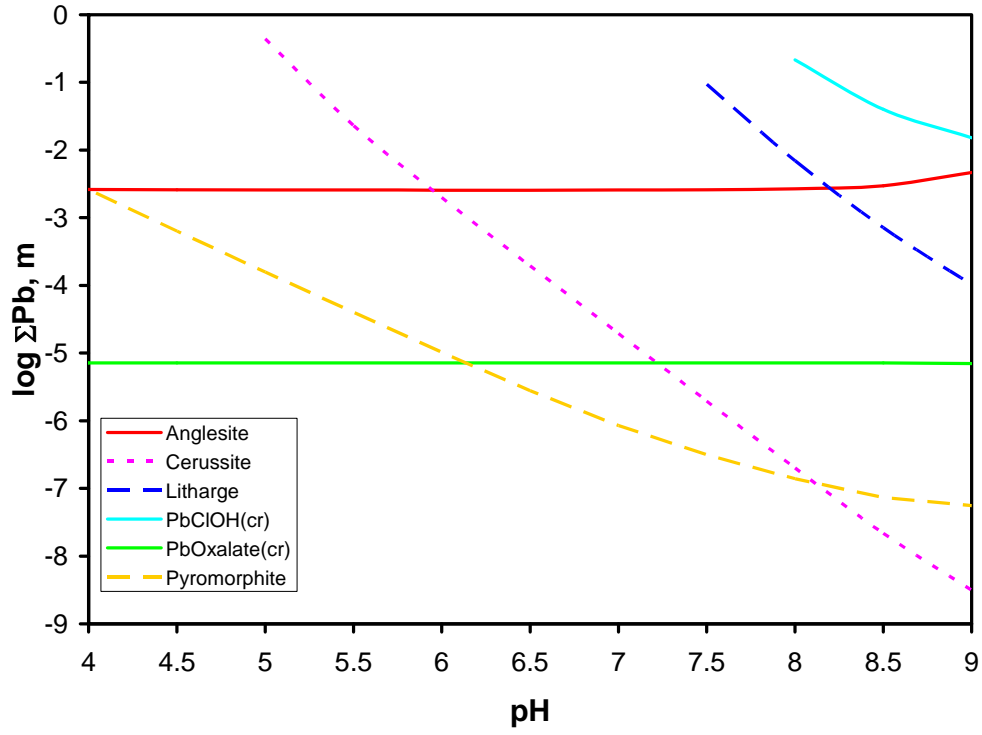
1
2 Figure 3
3
4
5



1
2
3
4
5
6

Figure 4

1



2

3

4

Figure 5

5