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Sandia National Laboratories
Waste Isolation Pilot Plant

Experimental determination of solubilities of lead oxalate (PbC_2O_4), di-calcium ethylenediaminetetraacetic acid ($Ca_2EDTA(s)$) in $MgCl_2$–H_2O system, and earlandite ($Ca_3[C_3H_5O(COO)_3]_2 \cdot 4H_2O$) in NaCl–$H_2O$ and $MgCl_2$–H_2O systems, and their respective Pitzer interaction parameters, Revision 1, Supersedes ERMS 564844

Work Carried Out under Tasks 23, 28, 29, 30, 31 and 35 of AP-154: Analysis Plan for Derivation of Thermodynamic Properties Including Pitzer Parameters for Solubility Studies of Iron, Lead and EDTA.
To be included in the AP-154 records package

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1 INTRODUCTION

This analysis report (AR) provides the results of derivation of thermodynamic properties including Pitzer parameters based on solubility of lead oxalate (PbC_2O_4) in $MgCl_2$ solutions (Task 23 under AP-154, Xiong, 2013a), di-calcium ethylenediaminetetraacetic acid ($Ca_2EDTA(s)$), $Ca_2C_{10}H_{12}N_2O_8(s)$, in $MgCl_2$ solutions (Task 30 under AP-154, Xiong, 2013a), and earlandite ($Ca_3[C_3H_5O(COO)_3]_2 \cdot 4H_2O$) in NaCl (Task 28 under AP-154, Xiong, 2013a) and $MgCl_2$ solutions (Task 35 under AP-154, Xiong, 2013a). In order to be consistent with the analysis for $MgCl_2$ solutions, this analysis also includes the revision of Tasks 29 and 31 for solubility of $Ca_2EDTA(s)$ in NaCl solutions, which was originally analyzed in Xiong (2012). The results reported in this Analysis Report will supersede Xiong (2012).

This analysis was carried out under Tasks 23, 28, 30, and 35 of AP-154, Revision 2 (Xiong, 2013b). The computer code EQ3/6 Version 8.0a (Wolery, 2008; Wolery et al., 2010; Xiong, 2011b) was used for this analysis. Wolery (2008), Wolery et al. (2010) and Xiong (2011b) completed the qualification of Version 8.0a of EQ3/6 according to Sandia National Laboratories' (SNL's) WIPP quality assurance (QA) procedures for WIPP compliance-related actinide solubility calculations, and US EPA approved it on September 27, 2011 (U.S. EPA, 2011).

Table 1 (see next page) defines the generic abbreviations, acronyms, and initialisms used in this report and other analysis reports.

This is the Revision 1 of Xiong (2015). The revision is required because α_1 was set as 2.0 in the confirmation runs, instead of the correct value of 1.4, required by AP-154, Revision 2 (Xiong, 2013b), for the following interaction pairs: Mg^{2+}—$CaEDTA^{2-}$, Ca^{2+}—$MgEDTA^{2-}$, Mg^{2+}—$EDTA^{4-}$, and Mg^{2+}—$[C_3H_5O(COO)_3]^{3-}$. After adding the correct values for α_1 for the above interactions, it showed that only the parameters for Mg^{2+}—$[C_3H_5O(COO)_3]^{3-}$ were affected. Therefore, the revision is restricted to the parameters related Mg^{2+}—$[C_3H_5O(COO)_3]^{3-}$ only.

Table 1. Abbreviations, Acronyms, and Initialisms.

Abbreviation, Acronym, or Initialism	Definition
acetate	CH_3COO^- or $CH_3CO_2^-$
Am, Am(III)	americium, americium in the +III oxidation state
am	amorphous
anhydrite	$CaSO_4$
AP	analysis plan
aq	aqueous
AR	analysis report
aragonite	$CaCO_3$, a polymorph of $CaCO_3$ that is metastable with respect to calcite
atm	atmosphere(s)
B, B(III)	boron, boron in the +III oxidation state
Br, Br(−I)	bromine, bromine in the −I oxidation state
brucite	$Mg(OH)_2$
C	carbon
Ca, Ca(II), Ca^{2+}	calcium, calcium in the +II oxidation state, calcium ion
calcite	$CaCO_3$, the thermodynamically stable polymorph of $CaCO_3$
citrate	$(CH_2COO)_2C(OH)(COO)^{3-}$ or $(CH_2CO_2)_2C(OH)(CO_2)^{3-}$
Cl, Cl(−I), Cl^-	chlorine, chlorine in the −I oxidation state, chloride ion
CMS	(Sandia/WIPP software) Configuration Management System
CO_2	carbon dioxide
CO_3^{2-}	carbonate
cr	crystaline
CRA-2009	the second WIPP Compliance Recertification Application, submitted to the EPA in March 2009
DB	(thermodynamic) database
DOE	(U.S.) Department of Energy
dolomite	$CaMg(CO_3)_2$, a carbonate mineral that is nucleates and grows slowly under low-temperature conditions and is often suppressed (prevented from forming) in geochemical modeling calculations
DRZ	disturbed rock zone
EDTA	ethylenediaminetetraacetate, $(CH_2COO)_2N(CH_2)_2N(CH_2COO)_2)^{4-}$ or $(CH_2CO_2)_2N(CH_2)_2N(CH_2CO_2)^{4-}$
EPA	(U.S.) Environmental Protection Agency
earlandite	$Ca_3[C_3H_5O(COO)_3]_2 \cdot 4H_2O$
EQ3/6	a geochemical software package for speciation and solubility calculations (EQ3NR) and reaction-path calculations (EQ6)

Table 1 continued on next page

Table 1. Abbreviations, Acronyms, and Initialisms (continued).

Abbreviation, Acronym, or Initialism	Definition
ERDA-6	Energy Research and Development Administration (WIPP Well) 6, a synthetic brine representative of fluids in Castile brine reservoirs
f_{CO_2}	fugacity (similar to the partial pressure) of CO_2
Fm.	Formation
FMT	Fracture-Matrix Transport, a geochemical speciation and solubility code
GWB	Generic Weep Brine, a synthetic brine representative of intergranular Salado brines at or near the stratigraphic horizon of the repository
gypsum	$CaSO_4 \cdot 2H_2O$
H or H_2, H^+	hydrogen or hydrogen ion
halite	NaCl
H_2O	water (aq, g, or contained in solid phases)
hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$
I	ionic strength
K, K(I)	potassium, potassium in the +I oxidation state
kg	kilogram(s)
M	molar
m	meter(s) or molal
magnesite	$MgCO_3$
Mg, Mg(II)	magnesium, magnesium in the +II oxidation state
MgO	magnesium oxide, used to refer to the WIPP engineered barrier, which includes periclase as the primary constituent and various impurities
mM	millimolar
Na, Na(I), Na^+	sodium, sodium in the +I oxidation state, sodium ion
nesquehonite	$MgCO_3 \cdot 3H_2O$
Np, Np(V)	neptunium, neptunium in the +V oxidation state
O or O_2	oxygen
OH, OH^-	hydroxide or hydroxide ion
oxalate	$(COO)^{2-}$ or $C_2O_4^{2-}$
PA	performance assessment
PABC	Performance Assessment Baseline Calculations

Table 1 continued on next page

Table 1. Abbreviations, Acronyms, and Initialisms (continued).

Abbreviation, Acronym, or Initialism	Definition
periclase	pure, crystalline MgO, the primary constituent of the WIPP engineered barrier
pH	the negative, common logarithm of the activity of H^+
pcH	the negative, common logarithm of the molar concentration of H^+
phase 3	$Mg_2Cl(OH)_3 \cdot 4H_2O$
phase 5	$Mg_3(OH)_5Cl \cdot 4H_2O$
pmH	the negative, common logarithm of the molal concentration of H^+
polyhalite	$K_2MgCa_2(SO_4)_4 \cdot 2H_2O$
QA	quality assurance
Rev.	revision
RH	relative humidity
S, S(VI), SO_4^{2-}	sulfur, sulfur in the +VI oxidation state, sulfate ion
s	solid
SCA	S. Cohen and Associates
SNL	Sandia National Laboratories
Th, Th(IV)	thorium, thorium in the +IV oxidation state
TIC	total inorganic C
WIPP	(U.S. DOE) Waste Isolation Pilot Plant
wt %	weight percent
μ^0/RT	dimensionless standard chemical potential

2 METHODS

The objective of this analysis report (AR) was to obtain the thermodynamic parameters including the Pitzer parameters in the systems Na^+—K^+—Mg^{2+}—Pb^{2+}—Cl^-—$C_2O_4^{2-}$, Na^+—Mg^{2+}—Ca^{2+}—Cl^-—$EDTA^{4-}$, and Na^+—Mg^{2+}—Ca^{2+}—Cl^-—$[C_3H_5O(COO)_3]^{3-}$ (or $Citrate^{3-}$), based on solubility data of PbC_2O_4(cr) in $MgCl_2$ solutions, of Ca_2EDTA(s) in $MgCl_2$ solutions, and of earlandite ($Ca_3[C_3H_5O(COO)_3]_2 \cdot 4H_2O$) in NaCl and $MgCl_2$ solutions, produced at SNL (Kirkes, Olivas, Jang, Kim, Xiong, 2014). Tables 2-6 list experimental data from that report.

In Xiong (2013a), solubility data of PbC_2O_4(cr) in NaCl solutions were evaluated, and a set of Pitzer parameters were obtained. In this AR, on the basis of Xiong (2013a) (Table 3), solubility data of PbC_2O_4(cr) in $MgCl_2$ solutions are evaluated to describe the interactions of lead species with the bulk electrolyte, $MgCl_2$.

The dissolution reaction for PbC_2O_4(cr) can be expressed as,

$$PbC_2O_4(cr) = Pb^{2+} + C_2O_4^{2-} \quad (1)$$

The corresponding solubility product constant of PbC_2O_4(cr) at infinite dilution can be cast as follows,

$$K_s^o = \frac{a_{Pb^{2+}} \times a_{C_2O_4^{2-}}}{a_{PbC_2O_4(cr)}} \quad (2)$$

The formation reaction for PbC_2O_4(aq) is written as,

$$Pb^{2+} + C_2O_4^{2-} = PbC_2O_4(aq) \quad (3)$$

The corresponding cumulative formation constant at infinite dilution is,

$$\beta_1^0 = \frac{a_{PbC_2O_4(aq)}}{a_{Pb^{2+}} \times a_{C_2O_4^{2-}}} \quad (4)$$

Similarly, the cumulative formation reaction for $Pb(C_2O_4)_2^{2-}$ can be written as,

$$Pb^{2+} + 2C_2O_4^{2-} = Pb(C_2O_4)_2^{2-} \quad (5)$$

The corresponding cumulative formation constant at infinite dilution should be,

$$\beta_2^0 = \frac{a_{Pb(C_2O_4)_2^{2-}}}{a_{Pb^{2+}} \times (a_{C_2O_4^{2-}})^2} \quad (6)$$

The experiments in this study were performed in a $MgCl_2$ medium and therefore complexation of Pb^{2+} with Cl^- needs to be considered in the modeling. Three lead-chloride aqueous complexes are considered: $PbCl^+$, $PbCl_2(aq)$, and $PbCl_3^-$. The cumulative formation reactions for these three complexes are as follows,

$$Pb^{2+} + Cl^- = PbCl^+ \quad (7)$$

$$Pb^{2+} + 2Cl^- = PbCl_2(aq) \quad (8)$$

$$Pb^{2+} + 3Cl^- = PbCl_3^- \quad (9)$$

The corresponding cumulative formation constants for lead-chloride complexes at infinite dilution are as follows,

$$\beta^0_{1,Cl} = \frac{a_{PbCl^+}}{a_{Pb^{2+}} \times a_{Cl^-}} \quad (10)$$

$$\beta^0_{2,Cl} = \frac{a_{PbCl_2(aq)}}{a_{Pb^{2+}} \times (a_{Cl^-})^2} \quad (11)$$

$$\beta^0_{3,Cl} = \frac{a_{PbCl_3^-}}{a_{Pb^{2+}} \times (a_{Cl^-})^3} \quad (12)$$

In this analysis report, the above cumulative formation constants for lead chloride species except for $\beta^0_{2,Cl}$ are taken from the literature (Table 8), and the formation constants for $PbC_2O_4(aq)$ and $Pb(C_2O_4)_2^{2-}$ are taken from Xiong (2013a) (Table 8). In the work of Xiong (2013a), the value of 2.03 for $\log \beta^0_{2,Cl}$ was taken from Millero and Byrne (1984). In the NaCl-H_2O system, the contribution from $PbCl_2(aq)$ to total lead concentrations is insignificant (please see EQ3/6 files in Xiong, 2013a). Therefore, $PbCl_2(aq)$ does not have an effect on the modeling in the NaCl-H_2O system. However, in the $MgCl_2$-H_2O system, $PbCl_2(aq)$ is one of the dominant contributors to total lead concentrations at $m_{MgCl_2} \geq 1.0$.

On the basis of Xiong (2013a), the experimental solubility data for $PbC_2O_4(cr)$ in $MgCl_2$ gathered under TP 08-02 (Table 2) were modeled to derive the Pitzer parameters for the interactions between Mg^{2+} and $PbCl_3^-$ and among Mg^{2+}, $PbCl^+$ and Cl^- (Table 8), with the aid of the computer code EQ3/6 Version 8.0a (Wolery et al., 2010; Xiong, 2011b).

The evaluation was performed by using the Python script (Task23_QA.py) (Table 7) which runs the EQ3CodeModule optimization routine (Kirchner, 2012) with EQ3NR input files PbCl2-1.3i through PbCl2-96.3i (Table 7). These input files are located in the folder labeled as "PbOxalate_MgCl2_QA" in the zip file "AP154_Tasks23&Others_DataPackage.zip" (Table 7).

The EQ3/6 provisional thermodynamic database (DB) DATA0.P23 (Table 7), which is modified from DATA0.FM1 (Xiong, 2011a), was used for this analysis. Please see Paul Domski's memos about details of data0.P23. The DATA0.P23 database is in AP154_Tasks23&Others_DataPackage.zip (Table 7), LIBAP154, in the CMS. All supporting EQ3/6 input and output (I/O) files for modeling solubility of lead oxalate in $MgCl_2$ solutions are also located in the above zip file. The path for those files is "/nfs/data/CVSLIB/WIPP_EXTERNAL/ap154/Files".

Table 2. Experimental results concerning solubility of $PbC_2O_4(s)$ in $MgCl_2$ solutions produced at SNL at 22.5 ± 0.5 °C for Task 23 under AP-154 (from Kirkes, Olivas, Jang, Kim, Xiong, 2014)*.

Experimental Number	Supporting Medium, $MgCl_2$, molal	Experimental time, days	pmH**	Solubility expressed as total lead on molal scale, $m_{\Sigma Pb}$
PbOx-0.01Mg-1	0.010	113	6.55	5.09E-05
PbOx-0.01Mg-2	0.010	113	6.06	4.20E-05
PbOx-0.1Mg-1	0.10	113	5.88	2.06E-04
PbOx-0.1Mg-2	0.10	113	5.88	2.05E-04
PbOx-1.0Mg-1	1.0	113	5.78	8.63E-04
PbOx-1.0Mg-2	1.0	113	5.79	9.24E-04
PbOx-1.5Mg-1	1.5	113	5.66	3.30E-03
PbOx-1.5Mg-2	1.5	113	5.65	3.31E-03
PbOx-2.0Mg-1	2.0	113	5.51	1.19E-02
PbOx-2.0Mg-2	2.0	113	5.49	1.16E-02
PbOx-2.5Mg-1	2.5	113	5.45	1.52E-02
PbOx-2.5Mg-2	2.5	113	5.43	1.70E-02
PbOx-0.01Mg-1	0.010	254	6.36	5.66E-05
PbOx-0.01Mg-2	0.010	254	6.17	4.62E-05
PbOx-0.1Mg-1	0.10	254	5.88	2.21E-04
PbOx-0.1Mg-2	0.10	254	5.89	1.99E-04
PbOx-1.0Mg-1	1.0	254	5.64	8.54E-04
PbOx-1.0Mg-2	1.0	254	5.72	8.43E-04
PbOx-1.5Mg-1	1.5	254	5.57	3.01E-03
PbOx-1.5Mg-2	1.5	254	5.58	2.89E-03
PbOx-2.0Mg-1	2.0	254	5.55	9.94E-03
PbOx-2.0Mg-2	2.0	254	5.54	1.00E-02
PbOx-2.5Mg-1	2.5	254	5.54	1.57E-02
PbOx-2.5Mg-2	2.5	254	5.45	1.50E-02
PbOx-0.01Mg-1	0.010	553	5.99	4.01E-05
PbOx-0.01Mg-2	0.010	553	6.20	4.00E-05
PbOx-0.1Mg-1	0.10	553	5.90	1.63E-04
PbOx-0.1Mg-2	0.10	553	5.89	1.65E-04
PbOx-1.0Mg-1	1.0	553	5.46	8.04E-04
PbOx-1.0Mg-2	1.0	553	5.55	8.25E-04
PbOx-1.5Mg-1	1.5	553	5.47	3.05E-03
PbOx-1.5Mg-2	1.5	553	5.45	2.82E-03

PbOx-2.0Mg-1	2.0	553	5.52	9.61E-03
PbOx-2.0Mg-2	2.0	553	5.52	9.54E-03
PbOx-2.5Mg-1	2.5	553	5.49	1.49E-02
PbOx-2.5Mg-2	2.5	553	5.42	1.47E-02
PbOx-0.01Mg-1	0.010	1059	6.04	4.69E-05
PbOx-0.01Mg-2	0.010	1059	6.18	4.65E-05
PbOx-0.1Mg-1	0.10	1059	5.97	1.74E-04
PbOx-0.1Mg-2	0.10	1059	5.96	1.77E-04
PbOx-1.0Mg-1	1.0	1059	5.65	1.03E-03
PbOx-1.0Mg-2	1.0	1059	5.68	1.02E-03
PbOx-1.5Mg-1	1.5	1059	5.59	3.25E-03
PbOx-1.5Mg-2	1.5	1059	5.50	3.32E-03
PbOx-2.0Mg-1	2.0	1059	5.60	1.07E-02
PbOx-2.0Mg-2	2.0	1059	5.58	1.11E-02
PbOx-2.5Mg-1	2.5	1059	5.56	1.63E-02
PbOx-2.5Mg-2	2.5	1059	5.49	1.62E-02
PbOx-0.01Mg-1	0.010	1107	6.14	4.69E-05
PbOx-0.01Mg-2	0.010	1107	6.33	4.67E-05
PbOx-0.1Mg-1	0.10	1107	6.12	1.81E-04
PbOx-0.1Mg-2	0.10	1107	6.08	1.81E-04
PbOx-1.0Mg-1	1.0	1107	5.65	1.08E-03
PbOx-1.0Mg-2	1.0	1107	5.71	1.06E-03
PbOx-1.5Mg-1	1.5	1107	5.61	3.64E-03
PbOx-1.5Mg-2	1.5	1107	5.52	3.44E-03
PbOx-2.0Mg-1	2.0	1107	5.63	1.19E-02
PbOx-2.0Mg-2	2.0	1107	5.62	1.19E-02
PbOx-2.5Mg-1	2.5	1107	5.63	1.82E-02
PbOx-2.5Mg-2	2.5	1107	5.56	1.79E-02
PbOx-0.01Mg-1	0.010	1155	6.09	4.73E-05
PbOx-0.01Mg-2	0.010	1155	6.35	4.71E-05
PbOx-0.1Mg-1	0.10	1155	6.00	1.97E-04
PbOx-0.1Mg-2	0.10	1155	6.03	1.95E-04
PbOx-1.0Mg-1	1.0	1155	5.72	1.02E-03
PbOx-1.0Mg-2	1.0	1155	5.79	1.09E-03
PbOx-1.5Mg-1	1.5	1155	5.71	3.71E-03
PbOx-1.5Mg-2	1.5	1155	5.56	3.55E-03
PbOx-2.0Mg-1	2.0	1155	5.74	1.13E-02

PbOx-2.0Mg-2	2.0	1155	5.72	1.27E-02
PbOx-2.5Mg-1	2.5	1155	5.72	1.99E-02
PbOx-2.5Mg-2	2.5	1155	5.61	2.00E-02
PbOx-0.01Mg-1	0.010	1211	5.96	4.57E-05
PbOx-0.01Mg-2	0.010	1211	6.22	4.60E-05
PbOx-0.1Mg-1	0.10	1211	6.09	1.85E-04
PbOx-0.1Mg-2	0.10	1211	6.08	1.84E-04
PbOx-1.0Mg-1	1.0	1211	5.73	9.93E-04
PbOx-1.0Mg-2	1.0	1211	5.76	1.02E-03
PbOx-1.5Mg-1	1.5	1211	5.67	3.50E-03
PbOx-1.5Mg-2	1.5	1211	5.55	3.54E-03
PbOx-2.0Mg-1	2.0	1211	5.67	1.21E-02
PbOx-2.0Mg-2	2.0	1211	5.68	1.36E-02
PbOx-2.5Mg-1	2.5	1211	5.68	1.65E-02
PbOx-2.5Mg-2	2.5	1211	5.62	1.58E-02
PbOx-0.01Mg-1	0.010	1358	5.92	4.38E-05
PbOx-0.01Mg-2	0.010	1358	6.25	4.64E-05
PbOx-0.1Mg-1	0.10	1358	6.10	1.69E-04
PbOx-0.1Mg-2	0.10	1358	6.15	1.72E-04
PbOx-1.0Mg-1	1.0	1358	5.74	9.57E-04
PbOx-1.0Mg-2	1.0	1358	5.79	1.03E-03
PbOx-1.5Mg-1	1.5	1358	5.68	3.42E-03
PbOx-1.5Mg-2	1.5	1358	5.54	3.22E-03
PbOx-2.0Mg-1	2.0	1358	5.71	1.12E-02
PbOx-2.0Mg-2	2.0	1358	5.63	1.08E-02
PbOx-2.5Mg-1	2.5	1358	5.65	1.71E-02
PbOx-2.5Mg-2	2.5	1358	5.62	1.72E-02

**In Kirkes, Olivas, Jang, Kim, Xiong (2014), pH reading were reported. Values of pmH reported in this analysis report are calculated by using the correction factors (A_M) for pH readings, and conversion factors (Θ) from molality to molarity, $pmH = pH_{ob} + A_M - \log \Theta$ (Xiong et al., 2010). The correction factors are from Hansen (2001). The conversion factors are from the EQ3 output files with the respective $MgCl_2$ concentrations. Please see the spreadsheet "AR_AP154_Tasks23,28,30,35_Modeling.xls".

Table 3. Experimental results concerning solubility of $Ca_2EDTA(s)$ in $MgCl_2$ solutions produced at SNL at 22.5 ± 0.5 °C for Task 30 under AP-154 (from Kirkes, Olivas, Jang, Kim, Xiong, 2014)*.

Experimental Number	Supporting Medium, $MgCl_2$, molal	Experimental time, days	pmH**	Solubility expressed as total calcium on molal scale, $m_{\Sigma Ca}$
Ca2EDTA-0.01MgCl2-1	0.010	767	7.88	7.27E-02
Ca2EDTA-0.01MgCl2-2	0.010	767	7.80	7.24E-02
Ca2EDTA-0.1MgCl2-1	0.10	767	7.78	1.10E-01
Ca2EDTA-0.1MgCl2-2	0.10	767	7.32	1.11E-01
Ca2EDTA-1.0MgCl2-1	1.0	767	7.49	1.74E-01
Ca2EDTA-1.0MgCl2-2	1.0	767	7.53	1.59E-01
Ca2EDTA-1.5MgCl2-1	1.5	767	7.38	2.10E-01
Ca2EDTA-1.5MgCl2-2	1.5	767	7.33	2.07E-01
Ca2EDTA-2.0MgCl2-1	2.0	767	7.34	2.24E-01
Ca2EDTA-2.0MgCl2-2	2.0	767	7.52	2.05E-01
Ca2EDTA-2.5MgCl2-1	2.5	767	7.45	2.96E-01
Ca2EDTA-2.5MgCl2-2	2.5	767	7.60	2.88E-01
Ca2EDTA-0.01MgCl2-1	0.010	941	7.72	8.06E-02
Ca2EDTA-0.01MgCl2-2	0.010	941	7.73	7.72E-02
Ca2EDTA-0.1MgCl2-1	0.10	941	7.77	1.18E-01
Ca2EDTA-0.1MgCl2-2	0.10	941	7.48	1.16E-01
Ca2EDTA-1.0MgCl2-1	1.0	941	7.57	1.84E-01
Ca2EDTA-1.0MgCl2-2	1.0	941	7.55	1.71E-01
Ca2EDTA-1.5MgCl2-1	1.5	941	7.60	2.28E-01
Ca2EDTA-1.5MgCl2-2	1.5	941	7.54	2.19E-01
Ca2EDTA-2.0MgCl2-1	2.0	941	7.62	2.29E-01
Ca2EDTA-2.0MgCl2-2	2.0	941	7.62	2.20E-01
Ca2EDTA-2.5MgCl2-1	2.5	941	7.68	3.04E-01
Ca2EDTA-2.5MgCl2-2	2.5	941	7.63	2.93E-01
Ca2EDTA-0.01MgCl2-1	0.010	1025	7.77	7.65E-02
Ca2EDTA-0.01MgCl2-2	0.010	1025	7.69	7.37E-02
Ca2EDTA-0.1MgCl2-1	0.10	1025	7.74	1.12E-01
Ca2EDTA-0.1MgCl2-2	0.10	1025	7.46	1.11E-01
Ca2EDTA-1.0MgCl2-1	1.0	1025	7.50	1.79E-01
Ca2EDTA-1.0MgCl2-2	1.0	1025	7.50	1.64E-01
Ca2EDTA-1.5MgCl2-1	1.5	1025	7.58	2.21E-01
Ca2EDTA-1.5MgCl2-2	1.5	1025	7.55	2.08E-01

Ca2EDTA-2.0MgCl2-1	2.0	1025	7.60	2.26E-01
Ca2EDTA-2.0MgCl2-2	2.0	1025	7.59	2.25E-01
Ca2EDTA-2.5MgCl2-1	2.5	1025	7.62	2.90E-01
Ca2EDTA-2.5MgCl2-2	2.5	1025	7.60	2.52E-01
Ca2EDTA-0.01MgCl2-1	0.010	1075	7.84	7.78E-02
Ca2EDTA-0.01MgCl2-2	0.010	1075	7.73	7.66E-02
Ca2EDTA-0.1MgCl2-1	0.10	1075	7.78	1.14E-01
Ca2EDTA-0.1MgCl2-2	0.10	1075	7.52	1.13E-01
Ca2EDTA-1.0MgCl2-1	1.0	1075	7.57	1.83E-01
Ca2EDTA-1.0MgCl2-2	1.0	1075	7.56	1.75E-01
Ca2EDTA-1.5MgCl2-1	1.5	1075	7.64	2.26E-01
Ca2EDTA-1.5MgCl2-2	1.5	1075	7.61	2.23E-01
Ca2EDTA-2.0MgCl2-1	2.0	1075	7.66	2.38E-01
Ca2EDTA-2.0MgCl2-2	2.0	1075	7.62	2.29E-01
Ca2EDTA-2.5MgCl2-1	2.5	1075	7.68	3.07E-01
Ca2EDTA-2.5MgCl2-2	2.5	1075	7.64	3.04E-01
Ca2EDTA-0.01MgCl2-1	0.010	1124	7.90	8.24E-02
Ca2EDTA-0.01MgCl2-2	0.010	1124	7.69	7.82E-02
Ca2EDTA-0.1MgCl2-1	0.10	1124	7.80	1.20E-01
Ca2EDTA-0.1MgCl2-2	0.10	1124	7.56	1.18E-01
Ca2EDTA-1.0MgCl2-1	1.0	1124	7.59	1.57E-01
Ca2EDTA-1.0MgCl2-2	1.0	1124	7.61	1.75E-01
Ca2EDTA-1.5MgCl2-1	1.5	1124	7.50	2.26E-01
Ca2EDTA-1.5MgCl2-2	1.5	1124	7.58	2.10E-01
Ca2EDTA-2.0MgCl2-1	2.0	1124	7.63	2.42E-01
Ca2EDTA-2.0MgCl2-2	2.0	1124	7.69	2.42E-01
Ca2EDTA-2.5MgCl2-1	2.5	1124	7.73	3.05E-01
Ca2EDTA-2.5MgCl2-2	2.5	1124	7.72	3.17E-01
Ca2EDTA-0.01MgCl2-1	0.010	1176	7.79	7.63E-02
Ca2EDTA-0.01MgCl2-2	0.010	1176	7.65	7.53E-02
Ca2EDTA-0.1MgCl2-1	0.10	1176	7.75	1.14E-01
Ca2EDTA-0.1MgCl2-2	0.10	1176	7.46	1.10E-01
Ca2EDTA-1.0MgCl2-1	1.0	1176	7.60	1.78E-01
Ca2EDTA-1.0MgCl2-2	1.0	1176	7.59	1.71E-01
Ca2EDTA-1.5MgCl2-1	1.5	1176	7.63	2.22E-01
Ca2EDTA-1.5MgCl2-2	1.5	1176	7.60	2.11E-01
Ca2EDTA-2.0MgCl2-1	2.0	1176	7.67	2.36E-01

Ca2EDTA-2.0MgCl2-2	2.0	1176	7.70	2.25E-01
Ca2EDTA-2.5MgCl2-1	2.5	1176	7.73	2.98E-01
Ca2EDTA-2.5MgCl2-2	2.5	1176	7.71	2.97E-01
Ca2EDTA-0.01MgCl2-1	0.010	1324	7.79	7.74E-02
Ca2EDTA-0.01MgCl2-2	0.010	1324	7.67	7.73E-02
Ca2EDTA-0.1MgCl2-1	0.10	1324	7.77	1.16E-01
Ca2EDTA-0.1MgCl2-2	0.10	1324	7.51	1.16E-01
Ca2EDTA-1.0MgCl2-1	1.0	1324	7.62	1.80E-01
Ca2EDTA-1.0MgCl2-2	1.0	1324	7.59	1.75E-01
Ca2EDTA-1.5MgCl2-1	1.5	1324	7.65	2.25E-01
Ca2EDTA-1.5MgCl2-2	1.5	1324	7.63	2.25E-01
Ca2EDTA-2.0MgCl2-1	2.0	1324	7.69	2.34E-01
Ca2EDTA-2.0MgCl2-2	2.0	1324	7.72	2.27E-01
Ca2EDTA-2.5MgCl2-1	2.5	1324	7.75	2.96E-01
Ca2EDTA-2.5MgCl2-2	2.5	1324	7.74	2.98E-01
Ca2EDTA-0.01MgCl2-1	0.010	1435	7.77	7.78E-02
Ca2EDTA-0.01MgCl2-2	0.010	1435	7.67	7.73E-02
Ca2EDTA-0.1MgCl2-1	0.10	1435	7.77	1.16E-01
Ca2EDTA-0.1MgCl2-2	0.10	1435	7.53	1.17E-01
Ca2EDTA-1.0MgCl2-1	1.0	1435	7.61	1.78E-01
Ca2EDTA-1.0MgCl2-2	1.0	1435	7.60	1.73E-01
Ca2EDTA-1.5MgCl2-1	1.5	1435	7.65	2.24E-01
Ca2EDTA-1.5MgCl2-2	1.5	1435	7.62	2.22E-01
Ca2EDTA-2.0MgCl2-1	2.0	1435	7.68	2.29E-01
Ca2EDTA-2.0MgCl2-2	2.0	1435	7.68	2.28E-01
Ca2EDTA-2.5MgCl2-1	2.5	1435	7.71	2.97E-01
Ca2EDTA-2.5MgCl2-2	2.5	1435	7.70	2.95E-01

**In Kirkes, Olivas, Jang, Kim, Xiong (2014), pH reading were reported. Values of pmH reported in this analysis report are calculated by using the correction factors (A_M) for pH readings, and conversion factors (Θ) from molality to molarity, $pmH = pH_{ob} + A_M - \log \Theta$ (Xiong et al., 2010). The correction factors are from Hansen (2001). The conversion factors are from the EQ3 output files with the respective $MgCl_2$ concentrations. Please see the spreadsheet "AR_AP154_Tasks23,28,30,35_Modeling.xls".

Table 4. Experimental results concerning solubility of $Ca_2EDTA(s)$ in NaCl solutions produced at SNL at 22.5 ± 0.5 °C for Task 29 under AP-154 (from Kirkes, Olivas, Jang, Kim, Xiong, 2014)*.

Experimental Number	Supporting Medium, NaCl, molal	Experimental time, days	pmH**	Solubility expressed as total calcium on molal scale, $m_{\Sigma Ca}$
Ca2EDTA-0.01-1	0.010	365	8.23	7.09E-02
Ca2EDTA-0.01-2	0.010	365	8.20	7.15E-02
Ca2EDTA-0.1-1	0.10	365	8.37	8.61E-02
Ca2EDTA-0.1-2	0.10	365	7.90	8.69E-02
Ca2EDTA-1.0-1	1.0	365	8.39	1.35E-01
Ca2EDTA-1.0-2	1.0	365	7.92	1.35E-01
Ca2EDTA-2.0-1	2.1	365	8.54	1.40E-01
Ca2EDTA-2.0-2	2.1	365	8.49	1.42E-01
Ca2EDTA-3.0-1	3.2	365	8.71	1.35E-01
Ca2EDTA-3.0-2	3.2	365	8.47	1.31E-01
Ca2EDTA-4.0-1	4.4	365	8.69	1.19E-01
Ca2EDTA-4.0-2	4.4	365	8.63	1.19E-01
Ca2EDTA-5.0-1	5.0	365	8.19	1.10E-01
Ca2EDTA-5.0-2	5.0	365	8.19	1.10E-01
Ca2EDTA-0.01-1	0.010	940	7.79	7.27E-02
Ca2EDTA-0.01-2	0.010	940	7.85	7.28E-02
Ca2EDTA-0.1-1	0.10	940	7.88	8.36E-02
Ca2EDTA-0.1-2	0.10	940	7.81	7.99E-02
Ca2EDTA-1.0-1	1.0	940	8.09	1.22E-01
Ca2EDTA-1.0-2	1.0	940	7.77	1.23E-01
Ca2EDTA-2.0-1	2.1	940	8.18	1.21E-01
Ca2EDTA-2.0-2	2.1	940	8.20	1.20E-01
Ca2EDTA-3.0-1	3.2	940	8.43	1.09E-01
Ca2EDTA-3.0-2	3.2	940	8.30	1.10E-01
Ca2EDTA-4.0-1	4.4	940	8.41	9.45E-02
Ca2EDTA-4.0-2	4.4	940	8.40	9.29E-02
Ca2EDTA-5.0-1	5.0	940	8.11	8.60E-02
Ca2EDTA-5.0-2	5.0	940	8.10	8.54E-02
Ca2EDTA-0.01-1	0.010	1025	7.84	7.30E-02
Ca2EDTA-0.01-2	0.010	1025	7.83	7.27E-02
Ca2EDTA-0.1-1	0.10	1025	7.81	8.49E-02
Ca2EDTA-0.1-2	0.10	1025	7.81	8.52E-02

Ca2EDTA-1.0-1	1.0	1025	8.00	1.22E-01
Ca2EDTA-1.0-2	1.0	1025	7.68	1.22E-01
Ca2EDTA-2.0-1	2.1	1025	8.13	1.21E-01
Ca2EDTA-2.0-2	2.1	1025	8.11	1.24E-01
Ca2EDTA-3.0-1	3.2	1025	8.23	1.10E-01
Ca2EDTA-3.0-2	3.2	1025	8.20	1.09E-01
Ca2EDTA-4.0-1	4.4	1025	8.37	9.28E-02
Ca2EDTA-4.0-2	4.4	1025	8.33	9.54E-02
Ca2EDTA-5.0-1	5.0	1025	8.14	9.02E-02
Ca2EDTA-5.0-2	5.0	1025	8.10	8.62E-02
Ca2EDTA-0.01-1	0.010	1074	7.88	7.33E-02
Ca2EDTA-0.01-2	0.010	1074	7.86	7.25E-02
Ca2EDTA-0.1-1	0.10	1074	7.90	8.42E-02
Ca2EDTA-0.1-2	0.10	1074	7.85	8.17E-02
Ca2EDTA-1.0-1	1.0	1074	8.03	1.23E-01
Ca2EDTA-1.0-2	1.0	1074	7.72	1.24E-01
Ca2EDTA-2.0-1	2.1	1074	8.13	1.22E-01
Ca2EDTA-2.0-2	2.1	1074	8.11	1.21E-01
Ca2EDTA-3.0-1	3.2	1074	8.25	1.08E-01
Ca2EDTA-3.0-2	3.2	1074	8.19	1.06E-01
Ca2EDTA-4.0-1	4.4	1074	8.33	9.24E-02
Ca2EDTA-4.0-2	4.4	1074	8.31	9.49E-02
Ca2EDTA-5.0-1	5.0	1074	8.14	8.43E-02
Ca2EDTA-5.0-2	5.0	1074	8.14	8.27E-02
Ca2EDTA-0.01-1	0.010	1124	7.94	7.24E-02
Ca2EDTA-0.01-2	0.010	1124	7.92	6.64E-02
Ca2EDTA-0.1-1	0.10	1124	7.96	8.39E-02
Ca2EDTA-0.1-2	0.10	1124	7.90	8.40E-02
Ca2EDTA-1.0-1	1.0	1124	8.02	1.21E-01
Ca2EDTA-1.0-2	1.0	1124	7.73	1.18E-01
Ca2EDTA-2.0-1	2.1	1124	8.09	1.21E-01
Ca2EDTA-2.0-2	2.1	1124	8.14	1.25E-01
Ca2EDTA-3.0-1	3.2	1124	8.35	1.10E-01
Ca2EDTA-3.0-2	3.2	1124	8.22	1.12E-01
Ca2EDTA-4.0-1	4.4	1124	8.34	9.76E-02
Ca2EDTA-4.0-2	4.4	1124	8.35	9.42E-02
Ca2EDTA-5.0-1	5.0	1124	8.23	8.16E-02
Ca2EDTA-5.0-2	5.0	1124	8.18	8.18E-02

Ca2EDTA-0.01-1	0.010	1172	7.86	7.10E-02
Ca2EDTA-0.01-2	0.010	1172	7.87	7.13E-02
Ca2EDTA-0.1-1	0.10	1172	7.90	8.46E-02
Ca2EDTA-0.1-2	0.10	1172	7.91	8.49E-02
Ca2EDTA-1.0-1	1.0	1172	8.00	1.22E-01
Ca2EDTA-1.0-2	1.0	1172	7.72	1.21E-01
Ca2EDTA-2.0-1	2.1	1172	8.10	1.19E-01
Ca2EDTA-2.0-2	2.1	1172	8.07	1.21E-01
Ca2EDTA-3.0-1	3.2	1172	8.23	1.06E-01
Ca2EDTA-3.0-2	3.2	1172	8.19	1.08E-01
Ca2EDTA-4.0-1	4.4	1172	8.31	9.39E-02
Ca2EDTA-4.0-2	4.4	1172	8.30	9.25E-02
Ca2EDTA-5.0-1	5.0	1172	8.19	8.54E-02
Ca2EDTA-5.0-2	5.0	1172	8.15	8.17E-02
Ca2EDTA-0.01-1	0.010	1323	7.85	7.31E-02
Ca2EDTA-0.01-2	0.010	1323	7.86	7.26E-02
Ca2EDTA-0.1-1	0.10	1323	7.88	8.55E-02
Ca2EDTA-0.1-2	0.10	1323	7.88	8.60E-02
Ca2EDTA-1.0-1	1.0	1323	7.99	1.24E-01
Ca2EDTA-1.0-2	1.0	1323	7.72	1.24E-01
Ca2EDTA-2.0-1	2.1	1323	8.11	1.22E-01
Ca2EDTA-2.0-2	2.1	1323	8.10	1.22E-01
Ca2EDTA-3.0-1	3.2	1323	8.23	1.12E-01
Ca2EDTA-3.0-2	3.2	1323	8.19	1.10E-01
Ca2EDTA-4.0-1	4.4	1323	8.33	9.55E-02
Ca2EDTA-4.0-2	4.4	1323	8.32	9.52E-02
Ca2EDTA-5.0-1	5.0	1323	8.20	7.94E-02
Ca2EDTA-5.0-2	5.0	1323	8.19	8.63E-02
Ca2EDTA-0.01-1	0.010	1431	7.88	7.32E-02
Ca2EDTA-0.01-2	0.010	1431	7.88	7.30E-02
Ca2EDTA-0.1-1	0.10	1431	7.85	8.54E-02
Ca2EDTA-0.1-2	0.10	1431	7.90	8.63E-02
Ca2EDTA-1.0-1	1.0	1431	7.98	1.22E-01
Ca2EDTA-1.0-2	1.0	1431	7.71	1.24E-01
Ca2EDTA-2.0-1	2.1	1431	8.07	1.22E-01
Ca2EDTA-2.0-2	2.1	1431	8.05	1.23E-01

Ca2EDTA-3.0-1	3.2	1431	8.17	1.11E-01
Ca2EDTA-3.0-2	3.2	1431	8.14	1.11E-01
Ca2EDTA-4.0-1	4.4	1431	8.24	9.55E-02
Ca2EDTA-4.0-2	4.4	1431	8.24	9.51E-02
Ca2EDTA-5.0-1	5.0	1431	8.12	7.69E-02
Ca2EDTA-5.0-2	5.0	1431	8.12	8.58E-02

**In Kirkes, Olivas, Jang, Kim, Xiong (2014), pH reading were reported. Values of pmH reported in this analysis report are calculated by using the correction factors (A_M) for pH readings, and conversion factors (Θ) from molality to molarity, $pmH = pH_{ob} + A_M - \log \Theta$ (Xiong et al., 2010). The correction factors are from Rai et al. (1995). The conversion factors are from the EQ3 output files with the respective NaCl concentrations. Please see the spreadsheet "AR_AP154_Tasks23,28,30,35_Modeling.xls".

Table 5. Experimental results concerning solubility of earlandite, $Ca_3[Citrate]_2 \cdot 4H_2O(s)$, in NaCl solutions produced at SNL at 22.5 ± 0.5 °C for Task 28 under AP-154 (from Kirkes, Olivas, Jang, Kim, Xiong, 2014)*.

Experimental Number	Supporting Medium, NaCl, molal	Experimental time, days	pmH**	Solubility expressed as total calcium on molal scale, $m_{\Sigma Ca}$
ACROS-ELDT-0.01-1	0.010	182	6.98	5.23E-03
ACROS-ELDT-0.01-2	0.010	182	6.96	5.39E-03
ACROS-ELDT-0.1-1	0.10	182	6.48	7.25E-03
ACROS-ELDT-0.1-2	0.10	182	6.54	7.89E-03
ACROS-ELDT-1.0-1	1.0	182	6.42	1.38E-02
ACROS-ELDT-1.0-2	1.0	182	6.51	1.86E-02
ACROS-ELDT-2.0-1	2.1	182	6.09	1.56E-02
ACROS-ELDT-2.0-2	2.1	182	6.12	1.56E-02
ACROS-ELDT-3.0-1	3.2	182	5.51	2.87E-02
ACROS-ELDT-3.0-2	3.2	182	5.29	3.00E-02
ACROS-ELDT-5.0-1	5.0	182	4.92	NA
ACROS-ELDT-5.0-2	5.0	182	4.89	NA
ACROS-ELDT-0.01-1	0.010	375	7.15	4.65E-03
ACROS-ELDT-0.01-2	0.010	375	7.27	5.02E-03
ACROS-ELDT-0.1-1	0.10	375	6.86	6.93E-03
ACROS-ELDT-0.1-2	0.10	375	6.99	6.67E-03
ACROS-ELDT-1.0-1	1.0	375	6.77	1.20E-02
ACROS-ELDT-1.0-2	1.0	375	6.39	1.24E-02
ACROS-ELDT-2.0-1	2.1	375	5.83	1.44E-02
ACROS-ELDT-2.0-2	2.1	375	6.30	1.39E-02
ACROS-ELDT-3.0-1	3.2	375	5.61	2.35E-02
ACROS-ELDT-3.0-2	3.2	375	5.39	2.58E-02
ACROS-ELDT-5.0-1	5.0	375	4.69	3.15E-02
ACROS-ELDT-5.0-2	5.0	375	4.73	3.35E-02
ACROS-ELDT-0.01-1	0.010	662	7.55	4.84E-03
ACROS-ELDT-0.01-2	0.010	662	7.54	4.73E-03
ACROS-ELDT-0.1-1	0.10	662	7.38	6.75E-03
ACROS-ELDT-0.1-2	0.10	662	7.46	6.75E-03
ACROS-ELDT-1.0-1	1.0	662	7.16	1.18E-02
ACROS-ELDT-1.0-2	1.0	662	6.59	1.17E-02
ACROS-ELDT-2.0-1	2.1	662	5.99	1.78E-02
ACROS-ELDT-2.0-2	2.1	662	6.06	1.73E-02

ACROS-ELDT-3.0-1	3.2	662	5.99	2.63E-02
ACROS-ELDT-3.0-2	3.2	662	5.59	2.65E-02
ACROS-ELDT-5.0-1	5.0	662	4.81	3.45E-02
ACROS-ELDT-5.0-2	5.0	662	4.81	3.47E-02
ACROS-ELDT-0.01-1	0.010	712	7.69	5.07E-03
ACROS-ELDT-0.01-2	0.010	712	7.70	4.97E-03
ACROS-ELDT-0.1-1	0.10	712	7.54	6.80E-03
ACROS-ELDT-0.1-2	0.10	712	7.61	6.90E-03
ACROS-ELDT-1.0-1	1.0	712	7.29	1.16E-02
ACROS-ELDT-1.0-2	1.0	712	6.62	1.19E-02
ACROS-ELDT-2.0-1	2.1	712	6.05	1.77E-02
ACROS-ELDT-2.0-2	2.1	712	6.13	1.74E-02
ACROS-ELDT-3.0-1	3.2	712	6.08	2.64E-02
ACROS-ELDT-3.0-2	3.2	712	5.62	2.67E-02
ACROS-ELDT-5.0-1	5.0	712	4.69	3.42E-02
ACROS-ELDT-5.0-2	5.0	712	4.67	3.41E-02
ACROS-ELDT-0.01-1	0.010	760	7.68	5.20E-03
ACROS-ELDT-0.01-2	0.010	760	7.65	5.04E-03
ACROS-ELDT-0.1-1	0.10	760	7.67	6.99E-03
ACROS-ELDT-0.1-2	0.10	760	7.64	6.79E-03
ACROS-ELDT-1.0-1	1.0	760	7.28	1.17E-02
ACROS-ELDT-1.0-2	1.0	760	6.57	1.20E-02
ACROS-ELDT-2.0-1	2.1	760	6.10	1.79E-02
ACROS-ELDT-2.0-2	2.1	760	6.17	1.73E-02
ACROS-ELDT-3.0-1	3.2	760	6.20	2.60E-02
ACROS-ELDT-3.0-2	3.2	760	6.13	2.61E-02
ACROS-ELDT-5.0-1	5.0	760	4.68	3.41E-02
ACROS-ELDT-5.0-2	5.0	760	4.69	3.40E-02
ACROS-ELDT-0.01-1	0.010	815	7.72	5.05E-03
ACROS-ELDT-0.01-2	0.010	815	7.71	4.87E-03
ACROS-ELDT-0.1-1	0.10	815	7.64	6.77E-03
ACROS-ELDT-0.1-2	0.10	815	7.64	6.39E-03
ACROS-ELDT-1.0-1	1.0	815	7.36	1.12E-02
ACROS-ELDT-1.0-2	1.0	815	6.63	1.17E-02
ACROS-ELDT-2.0-1	2.1	815	6.21	1.77E-02
ACROS-ELDT-2.0-2	2.1	815	6.30	1.75E-02
ACROS-ELDT-3.0-1	3.2	815	6.42	2.62E-02

ACROS-ELDT-3.0-2	3.2	815	5.75	2.59E-02
ACROS-ELDT-5.0-1	5.0	815	4.67	3.44E-02
ACROS-ELDT-5.0-2	5.0	815	4.68	3.25E-02
ACROS-ELDT-0.01-1	0.010	963	7.79	5.14E-03
ACROS-ELDT-0.01-2	0.010	963	7.86	5.06E-03
ACROS-ELDT-0.1-1	0.10	963	7.71	6.91E-03
ACROS-ELDT-0.1-2	0.10	963	7.72	6.93E-03
ACROS-ELDT-1.0-1	1.0	963	7.46	1.19E-02
ACROS-ELDT-1.0-2	1.0	963	6.58	1.19E-02
ACROS-ELDT-2.0-1	2.1	963	6.33	1.81E-02
ACROS-ELDT-2.0-2	2.1	963	6.41	1.81E-02
ACROS-ELDT-3.0-1	3.2	963	6.60	2.70E-02
ACROS-ELDT-3.0-2	3.2	963	6.02	2.72E-02
ACROS-ELDT-5.0-1	5.0	963	4.62	3.49E-02
ACROS-ELDT-5.0-2	5.0	963	4.63	3.47E-02
ACROS-ELDT-0.01-1	0.010	1067	7.95	5.20E-03
ACROS-ELDT-0.01-2	0.010	1067	7.94	5.14E-03
ACROS-ELDT-0.1-1	0.10	1067	7.81	6.98E-03
ACROS-ELDT-0.1-2	0.10	1067	7.82	6.91E-03
ACROS-ELDT-1.0-1	1.0	1067	7.59	1.19E-02
ACROS-ELDT-1.0-2	1.0	1067	6.65	1.20E-02
ACROS-ELDT-2.0-1	2.1	1067	6.48	1.84E-02
ACROS-ELDT-2.0-2	2.1	1067	6.54	1.82E-02
ACROS-ELDT-3.0-1	3.2	1067	6.69	2.70E-02
ACROS-ELDT-3.0-2	3.2	1067	6.38	2.71E-02
ACROS-ELDT-5.0-1	5.0	1067	4.62	3.49E-02
ACROS-ELDT-5.0-2	5.0	1067	4.65	3.44E-02

**In Kirkes, Olivas, Jang, Kim, Xiong (2014), pH reading were reported. Values of pmH reported in this analysis report are calculated by using the correction factors (A_M) for pH readings, and conversion factors (Θ) from molality to molarity, $pmH = pH_{ob} + A_M - \log \Theta$ (Xiong et al., 2010). The correction factors are from Rai et al. (1995). The conversion factors are from the EQ3 output files with the respective NaCl concentrations. Please see the spreadsheet "AR_AP154_Tasks23,28,30,35_Modeling.xls".

Table 6. Experimental results concerning solubility of earlandite, $Ca_3[Citrate]_2 \cdot 4H_2O(s)$, in $MgCl_2$ solutions produced at SNL at 22.5 ± 0.5 °C for Task 35 under AP-154 (from Kirkes, Olivas, Jang, Kim, Xiong, 2014)*.

Experimental Number	Supporting Medium, $MgCl_2$, molal	Experimental time, days	pmH**	Solubility expressed as total calcium on molal scale, $m_{\Sigma Ca}$
ACROS-ELDT-0.01 Mg-1	0.010	203	6.91	7.85E-03
ACROS-ELDT-0.01 Mg-2	0.010	203	6.99	7.87E-03
ACROS-ELDT-0.1 Mg-1	0.10	203	5.70	2.53E-02
ACROS-ELDT-0.1 Mg-2	0.10	203	5.70	2.32E-02
ACROS-ELDT-1.0 Mg-1	1.0	203	4.78	5.30E-02
ACROS-ELDT-1.0 Mg-2	1.0	203	4.79	5.11E-02
ACROS-ELDT-1.5 Mg-1	1.5	203	4.81	5.36E-02
ACROS-ELDT-1.5 Mg-2	1.5	203	4.84	5.34E-02
ACROS-ELDT-2.0 Mg-1	2.0	203	4.99	5.13E-02
ACROS-ELDT-2.0 Mg-2	2.0	203	5.33	5.24E-02
ACROS-ELDT-2.5 Mg-1	2.5	203	5.10	4.98E-02
ACROS-ELDT-2.5 Mg-2	2.5	203	4.86	4.93E-02
ACROS-ELDT-0.01 Mg-1	0.010	385	7.22	7.82E-03
ACROS-ELDT-0.01 Mg-2	0.010	385	7.38	7.69E-03
ACROS-ELDT-0.1 Mg-1	0.10	385	5.34	2.70E-02
ACROS-ELDT-0.1 Mg-2	0.10	385	5.36	2.66E-02
ACROS-ELDT-1.0 Mg-1	1.0	385	4.57	4.66E-02
ACROS-ELDT-1.0 Mg-2	1.0	385	4.69	4.64E-02
ACROS-ELDT-1.5 Mg-1	1.5	385	4.57	4.33E-02
ACROS-ELDT-1.5 Mg-2	1.5	385	4.56	4.56E-02
ACROS-ELDT-2.0 Mg-1	2.0	385	4.71	4.44E-02
ACROS-ELDT-2.0 Mg-2	2.0	385	5.10	4.57E-02
ACROS-ELDT-2.5 Mg-1	2.5	385	4.86	4.22E-02
ACROS-ELDT-2.5 Mg-2	2.5	385	4.41	4.26E-02
ACROS-ELDT-0.01 Mg-1	0.010	458	7.44	7.89E-03
ACROS-ELDT-0.01 Mg-2	0.010	458	7.62	7.87E-03
ACROS-ELDT-0.1 Mg-1	0.10	458	5.58	2.78E-02
ACROS-ELDT-0.1 Mg-2	0.10	458	5.62	2.87E-02
ACROS-ELDT-1.0 Mg-1	1.0	458	4.76	4.59E-02
ACROS-ELDT-1.0 Mg-2	1.0	458	4.81	4.56E-02
ACROS-ELDT-1.5 Mg-1	1.5	458	4.41	4.56E-02
ACROS-ELDT-1.5 Mg-2	1.5	458	4.63	4.59E-02

ACROS-ELDT-2.0 Mg-1	2.0	458	4.90	4.55E-02
ACROS-ELDT-2.0 Mg-2	2.0	458	5.05	4.59E-02
ACROS-ELDT-2.5 Mg-1	2.5	458	4.97	4.28E-02
ACROS-ELDT-2.5 Mg-2	2.5	458	4.60	4.27E-02
ACROS-ELDT-0.01 Mg-1	0.010	660	7.61	7.90E-03
ACROS-ELDT-0.01 Mg-2	0.010	660	7.67	7.58E-03
ACROS-ELDT-0.1 Mg-1	0.10	660	5.56	3.01E-02
ACROS-ELDT-0.1 Mg-2	0.10	660	5.56	3.07E-02
ACROS-ELDT-1.0 Mg-1	1.0	660	4.77	4.88E-02
ACROS-ELDT-1.0 Mg-2	1.0	660	4.81	4.87E-02
ACROS-ELDT-1.5 Mg-1	1.5	660	4.81	4.91E-02
ACROS-ELDT-1.5 Mg-2	1.5	660	4.82	4.89E-02
ACROS-ELDT-2.0 Mg-1	2.0	660	5.01	4.87E-02
ACROS-ELDT-2.0 Mg-2	2.0	660	5.39	4.87E-02
ACROS-ELDT-2.5 Mg-1	2.5	660	5.05	4.65E-02
ACROS-ELDT-2.5 Mg-2	2.5	660	4.71	4.62E-02
ACROS-ELDT-0.01 Mg-1	0.010	709	7.78	8.15E-03
ACROS-ELDT-0.01 Mg-2	0.010	709	7.78	8.04E-03
ACROS-ELDT-0.1 Mg-1	0.10	709	5.60	3.19E-02
ACROS-ELDT-0.1 Mg-2	0.10	709	5.61	3.14E-02
ACROS-ELDT-1.0 Mg-1	1.0	709	4.78	4.96E-02
ACROS-ELDT-1.0 Mg-2	1.0	709	4.80	4.91E-02
ACROS-ELDT-1.5 Mg-1	1.5	709	4.79	4.94E-02
ACROS-ELDT-1.5 Mg-2	1.5	709	4.79	4.79E-02
ACROS-ELDT-2.0 Mg-1	2.0	709	4.99	4.82E-02
ACROS-ELDT-2.0 Mg-2	2.0	709	5.07	4.98E-02
ACROS-ELDT-2.5 Mg-1	2.5	709	5.16	4.79E-02
ACROS-ELDT-2.5 Mg-2	2.5	709	4.72	4.85E-02
ACROS-ELDT-0.01 Mg-1	0.010	758	7.75	8.12E-03
ACROS-ELDT-0.01 Mg-2	0.010	758	7.78	7.78E-03
ACROS-ELDT-0.1 Mg-1	0.10	758	5.58	3.07E-02
ACROS-ELDT-0.1 Mg-2	0.10	758	5.57	3.16E-02
ACROS-ELDT-1.0 Mg-1	1.0	758	4.80	4.93E-02
ACROS-ELDT-1.0 Mg-2	1.0	758	4.94	4.75E-02
ACROS-ELDT-1.5 Mg-1	1.5	758	4.87	5.06E-02
ACROS-ELDT-1.5 Mg-2	1.5	758	4.76	4.99E-02
ACROS-ELDT-2.0 Mg-1	2.0	758	4.92	4.93E-02

ACROS-ELDT-2.0 Mg-2	2.0	758	5.25	5.06E-02
ACROS-ELDT-2.5 Mg-1	2.5	758	5.14	4.85E-02
ACROS-ELDT-2.5 Mg-2	2.5	758	4.63	4.75E-02
ACROS-ELDT-0.01 Mg-1	0.010	813	7.94	8.07E-03
ACROS-ELDT-0.01 Mg-2	0.010	813	7.76	7.85E-03
ACROS-ELDT-0.1 Mg-1	0.10	813	5.72	3.03E-02
ACROS-ELDT-0.1 Mg-2	0.10	813	5.73	3.19E-02
ACROS-ELDT-1.0 Mg-1	1.0	813	4.84	4.94E-02
ACROS-ELDT-1.0 Mg-2	1.0	813	4.88	4.91E-02
ACROS-ELDT-1.5 Mg-1	1.5	813	4.87	4.99E-02
ACROS-ELDT-1.5 Mg-2	1.5	813	4.86	4.99E-02
ACROS-ELDT-2.0 Mg-1	2.0	813	5.06	4.96E-02
ACROS-ELDT-2.0 Mg-2	2.0	813	5.43	4.98E-02
ACROS-ELDT-2.5 Mg-1	2.5	813	5.22	4.77E-02
ACROS-ELDT-2.5 Mg-2	2.5	813	4.79	4.73E-02
ACROS-ELDT-0.01 Mg-1	0.010	961	7.97	8.32E-03
ACROS-ELDT-0.01 Mg-2	0.010	961	7.97	8.06E-03
ACROS-ELDT-0.1 Mg-1	0.10	961	5.88	3.28E-02
ACROS-ELDT-0.1 Mg-2	0.10	961	5.89	3.31E-02
ACROS-ELDT-1.0 Mg-1	1.0	961	4.84	4.97E-02
ACROS-ELDT-1.0 Mg-2	1.0	961	4.88	4.96E-02
ACROS-ELDT-1.5 Mg-1	1.5	961	4.85	3.68E-02
ACROS-ELDT-1.5 Mg-2	1.5	961	4.86	5.02E-02
ACROS-ELDT-2.0 Mg-1	2.0	961	5.05	4.98E-02
ACROS-ELDT-2.0 Mg-2	2.0	961	5.43	4.97E-02
ACROS-ELDT-2.5 Mg-1	2.5	961	5.20	4.79E-02
ACROS-ELDT-2.5 Mg-2	2.5	961	4.77	4.76E-02

**In Kirkes, Olivas, Jang, Kim, Xiong (2014), pH reading were reported. Values of pmH reported in this analysis report are calculated by using the correction factors (A_M) for pH readings, and conversion factors (Θ) from molality to molarity, $pmH = pH_{ob} + A_M - \log \Theta$ (Xiong et al., 2010). The correction factors are from Hansen (2001). The conversion factors are from the EQ3 output files with the respective $MgCl_2$ concentrations. Please see the spreadsheet "AR_AP154_Tasks23,28,30,35_Modeling.xls".

Table 7. Locations of the Excel Spreadsheets, EQ3/6 I/O Files Associated with Calculations for This Analysis.

Description or Title of File(s)	Location of File(s)
Spreadsheet XIONG_Tasks23_28_30_35_AR.xls	In zip file AP154_Tasks23&Others_DataPackage.zip, /nfs/data/CVSLIB/WIPP_EXTERNAL/ap154/Files
EQ3/6 DB DATA0.P23	In zip file AP154_Tasks23&Others_DataPackage.zip, /nfs/data/CVSLIB/WIPP_EXTERNAL/ap154/Files
EQ3/6 I/O files: PbCl2-1.3i/o through PbCl2-96.3i/o Ca2ED-1.3i/o through Ca2ED-96.3i/o CaNa-1.3i/o through CaNa-112.3i/o EaNa-1.3i/o through EaNa-94.3i/o EaMg-1.3i/o through EaMg-96.3i/o CaClO4-1.3i/o through CaClO4-6.3i/o ClO4V-1.3i/o through ClO4V-6.3i/o	In zip file AP154_Tasks23&Others_DataPackage.zip, /nfs/data/CVSLIB/WIPP_EXTERNAL/ap154/Files
Python scripts: Task23_QA.py Task30_A_QA.py Task30_B_QA.py Tasks28&35_A_QA.py Tasks28&35_B_QA.py Tasks28&35_C_QA.py	In zip file AP154_Tasks23&Others_DataPackage.zip, /nfs/data/CVSLIB/WIPP_EXTERNAL/ap154/Files
Optimization result files: Results_Task23.txt Results_Task30_A.txt Results_Task30_B.txt Results_Tasks28&35_A.txt Results_Tasks28&35_B.txt Results_Tasks28&35_C.txt	In zip file AP154_Tasks23&Others_DataPackage.zip, /nfs/data/CVSLIB/WIPP_EXTERNAL/ap154/Files

As previously mentioned (Xiong, 2012), the solubility constant of $Ca_2EDTA(s)$ is important to performance assessment (PA). Regarding EDTA concentrations in the brines, the chemical equilibrium calculations involving species-containing EDTA supporting PA using the current WIPP thermodynamic database are inventory-limited. The addition of solubility constant for $Ca_2EDTA(s)$ into the WIPP thermodynamic database would make the concentrations of EDTA become solubility-limited, should the EDTA concentrations in inventories increase to a certain level to reach the saturation of $Ca_2EDTA(s)$.

The dissolution reaction for $Ca_2EDTA(s)$ can be expressed as,

$$Ca_2EDTA(s) = 2Ca^{2+} + EDTA^{4-} \quad (13)$$

The formation reaction for $CaEDTA^{2-}$ is written as follows,

$$Ca^{2+} + EDTA^{4-} = CaEDTA^{2-} \quad (14)$$

Based on solubilities of $Ca_2EDTA(s)$ expressed as total calcium concentrations from chemical analyses, the solubility constant (log K_{sp}) for Reaction (13) and the formation constant for Reaction (14) can be obtained by the computer modeling, and is recalculated in this analysis report (see Section 1).

The experimental solubility data for $Ca_2EDTA(s)$ in NaCl gathered under TP 08-02 were modelled to derive the log K_{sp} for $Ca_2EDTA(s)$ and the interaction between Na^+ and $CaEDTA^{2-}$ (Xiong, 2012).

In this work, in order that the sub-model based on solubility data in NaCl solutions be consistent with that based on solubility data in $MgCl_2$ solutions, solubility data of $Ca_2EDTA(s)$ in NaCl solutions are remodeled. In the modeling for the Na^+—Mg^{2+}—Ca^{2+}—Cl^-—$EDTA^{4-}$ system, using experimental solubility data of $Ca_2EDTA(s)$ in $MgCl_2$ solutions, the log K_{sp} and the interaction between Mg^{2+} and $EDTA^{4-}$ are modelled first. The value for log K_{sp} and the Pitzer parameter for the interaction between Mg^{2+} and $EDTA^{4-}$ are evaluated by using the Python script (Task30_A_QA.py) which runs the EQ3CodeModule optimization routine (Kirchner, 2012) with EQ3NR input files Ca2ED-1.3i through Ca2ED-96.3i. These files are located in the folder labeled as "Ca2EDTA_MgCl2_QA" in the zip file "AP154_Tasks23&Others_DataPackage.zip". Then, the formation constant for $CaEDTA^{2-}$ and the Pitzer parameters for the interaction between Na^+ and $CaEDTA^{2-}$ are evaluated using solubility data of $Ca_2EDTA(s)$ in NaCl solutions with EQ3NR input files CaNa-1.3i through CaNa-112.3i with the Python script Task30_B_QA.py. These files are located in the folder labeled as "Ca2EDTA_NaCl_QA" in the zip file "AP154_Tasks23&Others_DataPackage.zip".

Similarly, the solubility constant of earlandite is also important to PA, as citrate forms relatively strong complexes with actinides. Regarding citrate concentrations in the brines, the chemical equilibrium calculations involving species-containing citrate supporting PA using the current WIPP thermodynamic database are inventory-limited. The addition of solubility constant for earlandite into the WIPP thermodynamic database would make the concentrations of citrate become solubility-limited, should the citrate concentrations in inventories increase to a certain level to reach the saturation of earlandite.

The dissolution reaction for earlandite can be expressed as,

$$Ca_3[C_3H_5O(COO)_3]_2 \cdot 4H_2O \text{ (earlandite)} = 3Ca^{2+} + 2[C_3H_5O(COO)_3]^{3-} + 4H_2O \quad (15)$$

The formation reaction for $Ca[C_3H_5O(COO)_3]^-$ is written as follows,

$$Ca^{2+} + [C_3H_5O(COO)_3]^{3-} = Ca[C_3H_5O(COO)_3]^- \quad (16)$$

Based on solubilities of earlandite expressed as total calcium concentrations from chemical analyses, the solubility constant (log K_{sp}) for Reaction (15) and the formation constant for Reaction (16) can be obtained by the computer modeling.

In this work, the experimental solubility data for earlandite in NaCl and $MgCl_2$ solutions gathered under TP 08-02, in combination with the solubility data in $NaClO_4$ solutions from the literature (Ciavatta et al., 2001) are modelled to derive the log K_{sp} for earlandite and the respective interaction parameters between Na^+ and $Ca[C_3H_5O(COO)_3]^-$, and between Mg^{2+} and $Mg[C_3H_5O(COO)_3]^-$. First, the value for log K_{sp} and the Pitzer parameters in $MgCl_2$ solutions are evaluated by using the Python script Tasks28&35_A_QA.py. The EQ3NR input files include EaMg-1.3i through EaMg-96.3i for the solubility data in $MgCl_2$ solutions. Second, the formation constant and Pitzer parameters in NaCl solutions are evaluated by using the Python script Tasks28&35_B_QA.py with the EQ3NR input files, EaNa-1.3i through EaNa-94.3i for the solubility data in NaCl solutions. Third, the psi parameter, $\psi_{Na^+\text{-}Ca^{2+}\text{-}ClO_4^-}$, is evaluated by using the Python script Tasks28&35_C_QA.py with the EQ3NR input files, CaClO4-1.3i through CaClO4-6.3i for the solubility data in $NaClO_4$ solutions from Ciavitta et al. (2001). Notice that there are more than 72 data points in each solubility data set in NaCl and $MgCl_2$ solutions. However, because EQ3/6 allows only 150 input files as the maximum to be run in any single folder, only the first 72 data points from each set of the experimental data in NaCl and $MgCl_2$ solutions are used to generate EQ3NR input files. These files are located in the respective folders labeled as "Earlandite_NaCl_QA", "Earlandite_MgCl2_QA", and "Earlandite_NaClO4_QA" in the zip file "AP154_Tasks23&Others_DataPackage.zip".

3 RESULTS

Table 7 provides the complete set of thermodynamic parameters that accurately describe the solubility of lead oxalate in the system Na^+—K^+—Mg^{2+}—Pb^{2+}—Cl^-—$C_2O_4^{2-}$, based on modeling solubilities of lead oxalate in NaCl and $MgCl_2$ solutions produced at SNL Carlsbad Facility, and in $K_2C_2O_4$ solutions from the literature (see Xiong, 2013a). In Figure 1, experimental data concerning solubility of lead oxalate in $MgCl_2$ solutions are compared with

model predictions. It is clear from Figure 1 that the model can reproduce experimental data with high accuracy over the entire ionic strength range covered by the experimental studies.

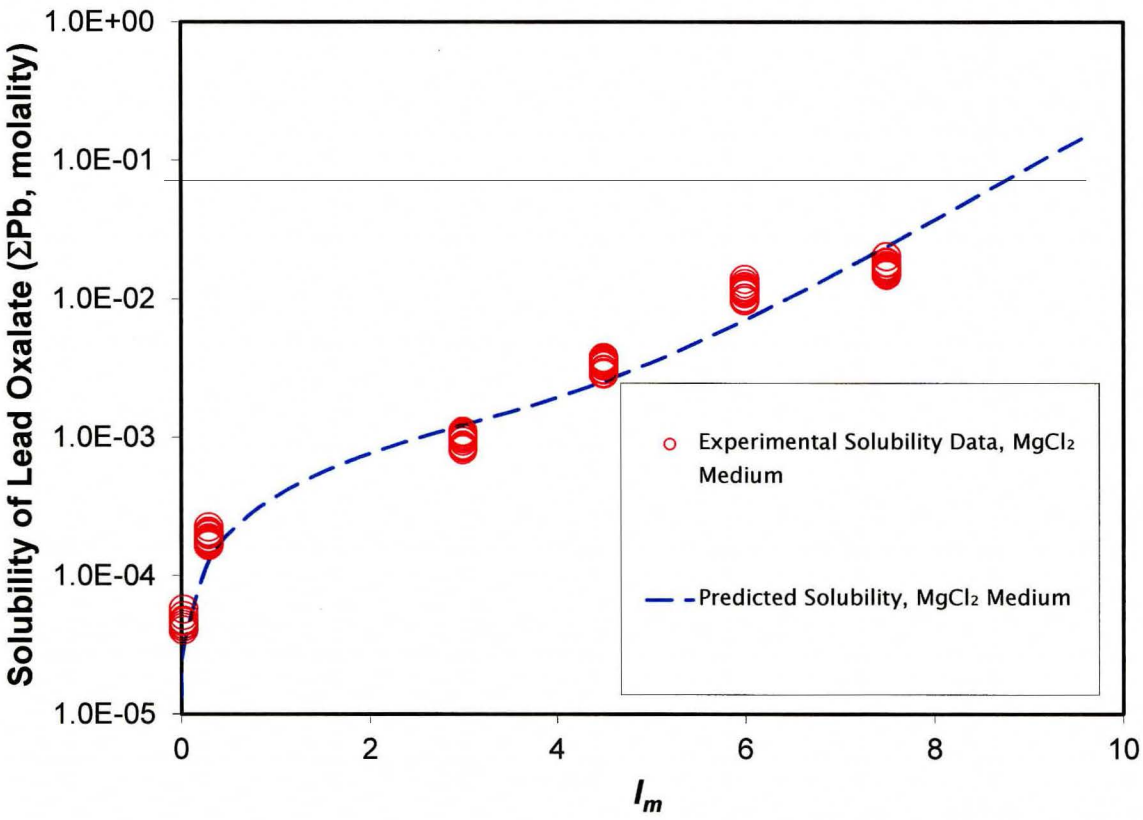

Figure 1. A plot showing comparisons of experimental solubilities of lead oxalate in $MgCl_2$ solutions with the model-predicted values.

Table 9 presents a set of the Pitzer parameters, log K_{sp} for $Ca_2EDTA(s)$, and log β_1 for $CaEDTA^{2-}$ in the system Na^+—Mg^{2+}—Ca^{2+}—Cl^-—$EDTA^{4-}$ determined in this AR. Notice that in the DATA0.FM1, the Pitzer interaction parameters for Na^+—$CaEDTA^{2-}$ are based on the analogs from Na^+—$MgEDTA^{2-}$. Similarly, the log β_1 for $CaEDTA^{2-}$ in DATA0.FM1 is also based on the analog to the log β_1 for $MgEDTA^{2-}$. Therefore, in addition to the log K_{sp} for $Ca_2EDTA(s)$, the model developed in this AR also refines the strength of the $CaEDTA^{2-}$ complex and the interactions between Na^+ and $CaEDTA^{2-}$. In Figure 2, experimental data for $Ca_2EDTA(s)$ in NaCl solutions are compared with model predictions. It is clear from Figure 2 that the model can reproduce experimental data with high accuracy over the entire ionic strength range covered by the experimental studies.

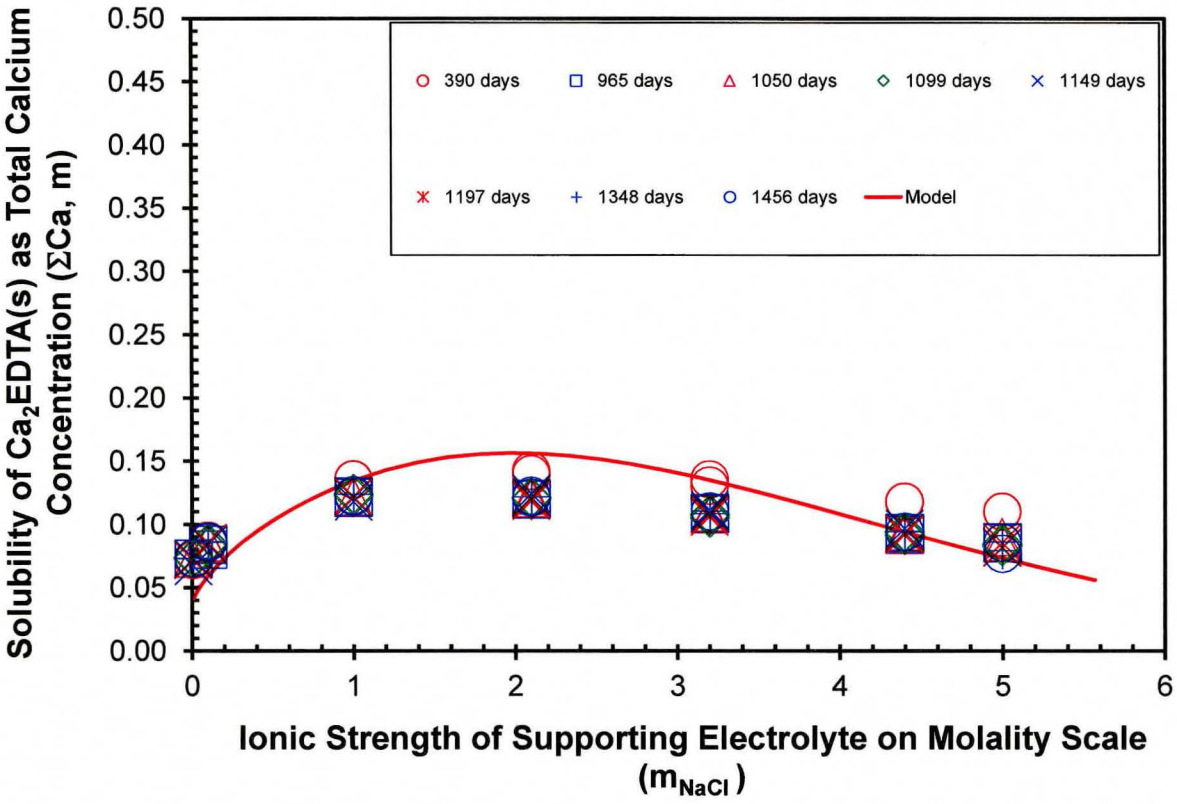

Figure 2. A plot showing comparisons of experimental solubilities of $Ca_2EDTA(s)$ in NaCl solutions with the model-predicted values.

Table 10 lists a set of thermodynamic parameters, including the Pitzer parameters, log K_{sp} for earlandite, and log β_1 for $Ca[C_3H_5O(COO)_3]^-$ in the system Na^+—Mg^{2+}—Ca^{2+}—Cl^-—$[C_3H_5O(COO)_3]^{3-}$ (or $Citrate^{3-}$) determined in this AR. Notice that in the DATA0.FM1, the Pitzer interaction parameters for Na^+—$Ca[C_3H_5O(COO)_3]^-$ are based on the analogs from Na^+—$Mg[C_3H_5O(COO)_3]^-$. Similarly, the log β_1 for $Ca[C_3H_5O(COO)_3]^-$ in DATA0.FM1 is also based on the analog to the log β_1 for $Mg[C_3H_5O(COO)_3]^-$. Therefore, in addition to the log K_{sp} for earlandite, the model developed in this AR also refines the formation constant for $Ca[C_3H_5O(COO)_3]^-$ and the interactions between Na^+ and $Ca[C_3H_5O(COO)_3]^-$.

Finally, the model developed in this study is tested regarding solubilities of earlandite in $NaClO_4$ solutions (Table 11). As indicated by Table 11, the model developed in this work can reproduce the experimental values with a precision that the predicted values differ less than 60% from the experimental values. The EQ3NR input and output files for the verification test are located in the folder "Earlandite_NaClO4_Verification_QA" in the zip file "AP154_Tasks23&Others_DataPackage.zip".

To the author's best knowledge, there are not published solubility data for $Ca_2EDTA(s)$, and an extensive literature search has not located any published solubility constants for

$Ca_2EDTA(s)$. Therefore, experimental solubility data in NaCl and $MgCl_2$ solutions produced at Sandia National Laboratories Carlsbad Facility and the thermodynamic parameters obtained based on these data would have a direct impact on PA. Incorporation of the thermodynamic parameters obtained in this analysis would make EDTA concentrations in brines become solubility-limited, should EDTA concentrations calculated from the inventory exceed the solubility limit of $Ca_2EDTA(s)$.

In the same token, incorporation of the thermodynamic parameters related to earlandite derived in this AR into the WIPP thermodynamic database would also make citrate concentrations in brines become solubility-controlled, should citrate concentrations calculated from the inventory be higher than the solubility limit of earlandite. Notice that the log K_{sp}, -18.11, for earlandite obtained in this AR, is identical to the literature value of -18.11 (Ciavatta et al., 2001), which was adopted for the previous analysis (Xiong, 2006). As the log K_{sp} obtained by Ciavatta et al. (2001) is independent, the excellent agreement of the log K_{sp} determined by this AR with that of the literature value provides additional credits for the Pitzer parameters derived by this AR for the system.

Table 8. Equilibrium constants at infinite dilution, 25°C and 1 bar, Pitzer interaction parameters in the Na^+—K^+—Mg^{2+}—Pb^{2+}—Cl^-—$C_2O_4^{2-}$ system

Reactions	log K_s^o, log β_1^o, or log β_2^o	Reference and Remarks
$PbC_2O_4(cr) = Pb^{2+} + C_2O_4^{2-}$	−11.13 ± 0.15 (2σ)	Xiong (2013a)
$Pb^{2+} + C_2O_4^{2-} = PbC_2O_4(aq)$	5.85 ± 0.10 (2σ)	Xiong (2013a)
$Pb^{2+} + 2C_2O_4^{2-} = Pb(C_2O_4)_2^{2-}$	8.05 ± 0.15 (2σ)	Xiong (2013a)
$Pb^{2+} + Cl^- = PbCl^+$	1.48	Millero and Byrne (1984)
$Pb^{2+} + 2Cl^- = PbCl_2(aq)$	2.03	Millero and Byrne (1984)
$Pb^{2+} + 3Cl^- = PbCl_3^-$	1.86	Millero and Byrne (1984)

Pitzer Binary Interaction Parameters

Species *i*	Species *j*	$\beta^{(0)}$	$\beta^{(1)}$	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	Xiong (2013a)
Mg^{2+}	$PbCl_3^-$	1.4277	1.74	0	This work
K^+	$Pb(C_2O_4)_2^{2-}$	0	−1.86	0.198	Xiong (2013a)
Na^+	$Pb(C_2O_4)_2^{2-}$	0	−1.86	0.198	Xiong (2013a)

Pitzer Mixing Interaction Parameters and Interaction Parameters Involving Neutral Species

Species *i*	Species *j*	Species *k*	λ_{ij} or θ_{ij}	ζ_{ijk}/Ψ_{ijk}	
Cl^-	$PbCl_2(aq)$		−0.14		Xiong (2013a)
Na^+	$PbCl_2(aq)$		−0.11		Felmy et al. (2000)
Cl^-	$PbCl_3^-$		0.7371		This work
Na^+	Pb^{2+}		0.10		Felmy et al. (2000)
Na^+	$PbCl_2(aq)$	Cl^-		0	Xiong (2013a)
Mg^{2+}	$PbCl^+$	Cl^-	0	−0.4129	This work
Mg^{2+}	MgOxalate(aq)	0.7454			This work
Na^+	$PbC_2O_4(aq)$	Cl^-	0	0	Xiong (2013a)

Table 9. Equilibrium constants at infinite dilution, 25°C and 1 bar, and Pitzer interaction parameters in the Na^+—Mg^{2+}—Ca^{2+}—Cl^-—$EDTA^{4-}$ system

Pitzer Parameters					
Species, *i*	Species, *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	References
Na^+	$CaEDTA^{2-}$	–0.00956 [B]	1.74 [A]	0.0131 [B]	This work
Mg^{2+}	$CaEDTA^{2-}$	0.525 [C]	3.27 [A]	0	This work [E]
Ca^{2+}	$MgEDTA^{2-}$	0.08436 [C]	3.27 [A]	0	This work [E]
Mg^{2+}	$EDTA^{4-}$	–0.01 [C]	11.6 [D]	0.3 [C]	This work [E]
Equilibrium Constants for Dissolution Reaction for $Ca_2EDTA(s)$ and Formation Reaction for $CaEDTA^{2-}$					
Reaction			log K_{sp} and log β_1 at 25 °C		
$Ca_2EDTA(s) = 2Ca^{2+} + EDTA^{4-}$			–15.39		This work
$Ca^{2+} + EDTA^{4-} = CaEDTA^{2-}$			11.16		This work

[A] Values are set according to AP-154, Revision 2 (Xiong, 2013b).
[B] These values correspond to those at Iteration 478 in Results_Task30_B.txt.
[C] This value corresponds to those at Iteration 5 in Results_Task30_A.txt.
[D] The $\beta^{(1)}$ is set to 11.6 according to AP-154, Revision 2 (Xiong, 2013b) for 1:4 and 4:1 interactions in combination with setting $\alpha_1 = 1.4$ in analog to α_1 for the Th^{4+}—SO_4^{2-} interaction.
[E] In the modeling, $\beta^{(2)}$ for these interactions are not modeled.

Table 10. Equilibrium constants at infinite dilution, 25°C and 1 bar, Pitzer interaction parameters in the Na^+—Mg^{2+}—Ca^{2+}—Cl^-—$[C_3H_5O(COO)_3]^{3-}$ (or $Citrate^{3-}$) system

Pitzer Parameters					
Species, *i*	Species, *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	References
Na^+	$Ca[C_3H_5O(COO)_3]^-$	–0.1310	0.29 [A]	–0.006818	This work
Mg^{2+}	$Mg[C_3H_5O(COO)_3]^-$	1.0915	1.74 [A]	0	This work
Mg^{2+}	$Ca[C_3H_5O(COO)_3]^-$	0.3760	1.74 [A]	0	This work
Mg^{2+}	$[C_3H_5O(COO)_3]^{3-}$	0.9330	4.4 [B]	0	This work [C]
Pitzer Mixing Interaction Parameters					
Species *i*	Species *j*	Species *k*	θ_{ij}	ψ_{ijk}	References
Na^+	Ca^{2+}	ClO_4^-	0.07	0.1574	θ_{ij} from data0.fm1; ψ_{ijk} from this work
Equilibrium Constants for Dissolution Reaction of Earlandite and Formation Reaction for $Ca[C_3H_5O(COO)_3]^-$					
Reaction			log K_{sp} and log β_1 at 25 °C		References
$Ca_3[C_3H_5O(COO)_3]_2 \cdot 4H_2O$ (earlandite) = $3Ca^{2+}$ + $2[C_3H_5O(COO)_3]^{3-}$ + $4H_2O$			–18.1061		This work
Ca^{2+} + $[C_3H_5O(COO)_3]^-$ = $Ca[C_3H_5O(COO)_3]^-$			4.9730		This work

[A] Values are set according to AP-154, Revision 2 (Xiong, 2013b).
[B] The value for $\beta^{(1)}$ is set to 4.4 based on the analog to that for the Mg^{2+}—$NpO_2(CO_3)_2^{3-}$ interaction from FM1.DATA0, which originated from Al Mahamid et al. (1998).
[C] In the modeling, $\beta^{(2)}$ for this interaction is not modeled.

Table 11. Comparison of solubility data of earlandite in $NaClO_4$ solutions from Ciavatta et al. (2001) with those predicted by the model developed by this work (model validation test).

Ionic Strength, molal	Σm_{Ca}, Experimental	Σm_{Ca}, Model	Difference in %
0.10	6.20E-03	6.77E-03	-9.24
0.25	6.51E-03	8.80E-03	-35.15
0.51	7.31E-03	1.06E-02	-45.21
1.05	7.91E-03	1.25E-02	-58.52
2.21	8.58E-03	1.05E-02	-22.22
3.50	9.32E-03	6.85E-03	26.52

4 CONCLUSIONS

In this AR, thermodynamic parameters including dissolution constants for $Ca_2EDTA(s)$ and earlandite, complex formation constants for $CaEDTA^{2-}$ and $Ca[C_3H_5O(COO)_3]^-$, and Pitzer interaction parameters, are obtained, based on solubility data of lead oxalate, di-calcium ethylenediaminetetraacetic acid in $MgCl_2$ solutions, and earlandite in NaCl and $MgCl_2$ solutions. In combination with the other parameters evaluated under AP-154, these parameters would enable us to accurately model the interactions among the organic ligands, dissolved Fe(II) and Pb(II) in concentrated brines including the WIPP brines. In addition, incorporation of the thermodynamic parameters related to $Ca_2EDTA(s)$ and earlandite derived in this AR into the WIPP thermodynamic database would make EDTA and citrate concentrations in brines become solubility-controlled, should EDTA and citrate concentrations calculated from the inventory be higher than the respective solubility limits of $Ca_2EDTA(s)$ and earlandite.

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