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Sandia National Laboratories
Waste Isolation Pilot Plant

Experimental and Thermodynamic Modeling of $PbEDTA^{2-}$ Interactions in NaCl and $MgCl_2$ Solutions

Work Carried Out under Tasks 18 and 19 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

The Waste Isolation Pilot Plant (WIPP) is a U.S. Department of Energy (DOE) repository in southeast New Mexico for defense-related transuranic (TRU) waste. The repository, which opened in March 1999, is located at a subsurface depth of 655 m in the Salado Fm., a Permian bedded-salt formation. It is planned to use a significant amount of lead as a radiation-shielding material for wastes with significant γ-radiation placed in the WIPP.

Ethylenediaminetetraacetate, $(CH_2COO)_2N(CH_2)_2N(CH_2COO)_2)^{4-}$, abbreviated as $EDTA^{4-}$, is one of the organic ligands present in the waste stream that has important impact to the Performance Assessment (PA). When it is dissolved in the WIPP brines such as Generic Weep Brine (GWB) from the Salado Fm. at the stratigraphic horizon of the repository, and Energy Research and Development Administration (WIPP Well) 6 (ERDA-6) from the underlying Castile Fm., it can form strong complexes with actinides, increasing the mobile fraction of actinides. On the other hand, lead also forms a strong complex with $EDTA^{4-}$. Consequently, the lead-EDTA complex, $PbEDTA^{2-}$, would strongly compete with actinides for soluble $EDTA^{4-}$, which would decrease the mobile fraction of actinides. Therefore, the accurate knowledge of the interactions of $PbEDTA^{2-}$ with major ions in the WIPP brines in a wide range of ionic strengths has important bearings on the chemical behavior in the repository.

This analysis report (AR) provides the results of derivation of thermodynamic properties including Pitzer parameters based on solubility of litharge (PbO) in NaCl and $MgCl_2$ solutions in the presence of $EDTA^{4-}$.

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 (US EPA, 2011).

This analysis was carried out under Tasks 18 and 19 of AP-154, Revision 2 (Xiong, 2013b).

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

Table 1. Abbreviations, acronyms, and initialisms.

Abbreviation, Acronym, or Initialism	Definition
a	activity
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
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
β_{mn}	cumulative formation constant at infinite dilution with "m" number of the complexing ligand *A* and "n" number of the complexing ligand *B* in case that there are two complexing ligands
β_n	cumulative formation constant at infinite dilution with "n" number of the complexing ligand *A* in case that there is only one complexing ligand
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 $CaCO_3$
cerussite	$PbCO_3$(cr)
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
CRA-2009	the second WIPP Compliance Recertification Application, submitted to the EPA in March 2009
DB	(thermodynamic) database
DOE	(U.S.) Department of Energy

Table 1 continued on next page

Table 1. Abbreviations, acronyms, and initialisms (continued).

Abbreviation, Acronym, or Initialism	Definition
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
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
EQ3/6	a geochemical software package for speciation and solubility calculations (EQ3NR) and reaction-path calculations (EQ6)
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)
K_s^o	solubility constant at infinite dilution
Litharge	PbO(cr)
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	$(COO)_2^{2-}$ or $C_2O_4^{2-}$

Table 1 continued on next page

Table 1. Abbreviations, acronyms, and initialisms (continued).

Abbreviation, Acronym, or Initialism	Definition
PA	performance assessment
PABC	Performance Assessment Baseline Calculations
Pb, Pb(II), Pb^{2+}	lead, lead in the +II oxidation state, lead ion
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	$Mg_3(OH)_5Cl \cdot 4H_2O$
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 was to derive thermodynamic properties in the Na^+—Mg^{2+}—Pb^{2+}—Cl^-—$EDTA^{4-}$ system based on solubility data of litharge (PbO(cr)) in NaCl and $MgCl_2$ solutions produced at SNL (Jang, Xiong, Kim, and Nemer, 2012). Tables 2 and 3 list experimental data in NaCl, and in $MgCl_2$ solutions from the above report, respectively.

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

$$PbO(cr) + 2H^+ = Pb^{2+} + H_2O \quad (1)$$

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

$$K^o_{s2} = \frac{a_{Pb^{2+}} \times a_{H_2O}}{a_{PbO(cr)} \times a^2_{H^+}} \quad (2)$$

In this analysis, the aqueous lead species included are Pb^{2+}, $PbCl^+$, $PbCl_2(aq)$, $PbCl_3^-$, and $PbEDTA^{2-}$. In the Analysis Report for lead oxalate, Pb^{2+}, $PbCl^+$, $PbCl_2(aq)$, $PbCl_3^-$ have been incorporated and the sources for them have been cited (Xiong, 2013a). Therefore, their citations will not be repeated in this Analysis Report.

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

$$Pb^{2+} + EDTA^{4-} = PbEDTA^{2-} \quad (3)$$

The corresponding formation constant at infinite dilution is,

$$\beta^0_1 = \frac{m_{PbEDTA^{2-}}}{m_{Pb^{2+}} \times m_{EDTA^{4-}}} \times \frac{\gamma_{PbEDTA^{2-}}}{\gamma_{Pb^{2+}} \times \gamma_{EDTA^{4-}}} = \frac{a_{PbEDTA^{2-}}}{a_{Pb^{2+}} \times a_{EDTA^{4-}}} \quad (4)$$

In this analysis report, the log K^o_{s2} for Reaction (1) is taken from ymp.R2/ymp.R0 (Table 4). In the review performed by Andregg (1977), the author recommended a value of 18.30 ± 0.21 in logarithmic unit at an ionic strength of 0.1 M and 20°C for the formation constant for Reaction (3). In the work of Uhler and Helz (1984), they obtained a value of 17.42 ± 0.06 at an ionic strength of 0.16 M and 25°C. In this work, the value recommended by Andregg (1977) is extrapolated to infinite dilution by using the Davies equation,

$$\log \gamma_i = -A_\gamma z_i^2 \left(\frac{\sqrt{I_m}}{1+\sqrt{I_m}} + 0.2 I_m\right) \quad (5)$$

where γ_i is the activity coefficient of species i, A_γ the Debye-Hükel slope for activity coefficient, which is 0.5092 at 25°C from Helgeson and Kirkham (1974), z_i the charge of species i, and I_m ionic strength on molal scale. Notice that the $\log \beta_1^o$ of 20.42 ± 0.21 (2σ) is based on the calculation for the value of Andregg (1977) (Table 4). Similarly, based on the value of Uhler and Helz (1984), the $\log \beta_1^o$ is 20.01 ± 0.20 (2σ). Using these two values as baselines, the $\log \beta_1^o$ is varied from 20.42 to 20.00 in the simulations for deciding which value should be selected. The simulations indicate that the residuals slightly decrease when $\log \beta_1^o$ changes from 20.24 to 20.00, when other parameters remain constant (please compare Iteration 1 for Results_logK=20.42.txt, Results_logK=20.20.txt, Results_logK=20.10.txt, and Results_logK=20.0009.txt). Therefore, $\log \beta_1^o$ of 20.00 is selected, and it is identical to the value calculated from that of Uhler and Helz (1984) when the uncertainties are taken into consideration.

Using experimental solubility data of PbO(cr) in NaCl solutions and $MgCl_2$ solutions from this work, the Pitzer parameters associated with $PbEDTA^{2-}$ are modeled using EQ3/6 Version 8.0a (Tables 4 and 5) with the Python script (Kirchner, 2012).

In the modeling, the experimental data in NaCl solutions are employed to generate EQ3 files from EDNa-1.3i through EDNa-75.3i. Similarly, the experimental data in $MgCl_2$ solutions are used to produce EQ3 input files from PbEB-1.3i through PbEB-75.3i. Notice that there are more than 75 data points in the experimental sets in both NaCl and $MgCl_2$ solutions. However, only the first 75 data points are used to generate the EQ3 input files. The reason for doing this is that the maximum allowable input files in a folder are 150 input files in running all EQ3 input files within one folder using a wild card (i.e., *.3i), which is adapted in the Python script. Therefore, the EQ3 input files from the experimental set in NaCl solutions (75 input files in subtotal) are combined with those from the experimental set in $MgCl_2$ solutions (75 in subtotal) to simultaneously fit the required parameters, resulting in 150 input files in total. The parameters obtained in this analysis are tabulated in Tables 4 and 5. Notice that the parameters obtained correspond to those at Iteration 44 (see Results_data0P18_08-25-14_XYL.txt, and Results_PD_08-21-14.txt). Those parameters are selected based on the following constraint and consideration. In this suite of EQ3 input files, when the Python script changes the targeted parameters to certain values, some of input files create a convergence problem before the optimization is completed. In the Paul Domski's official run (Results_PD_08-21-14.txt) and my unofficial run for comparison (Results_data0P18_08-25-14_XYL.txt), the parameters are reproducible until Iteration 44. Therefore, the parameters at the last reproducible iteration (i.e., Iteration 44) are selected.

Table 2. Experimental results concerning solubility of PbO(cr) in NaCl solutions produced at SNL at 22.5 ± 1.5 °C (from Jang, Xiong, Kim, and Nemer, 2012)*.

Experimental number	day	ΣPb, mol•kg^{-1}	ΣNa^{B}, mol•kg^{-1}	ΣCl^{B}, mol•kg^{-1}	pmH^{A}	ΣEDTA^{B}, mol•kg^{-1}	ΣMg^{B}, mol•kg^{-1}
Mg2EDTA-0.01-2	848	1.07E-01	0.01	0.01	10.63	0.15	0.29
Mg2EDTA-0.1-1	848	1.01E-01	0.09	0.09	10.83	0.15	0.29
Mg2EDTA-0.1-2	848	9.71E-02	0.09	0.09	10.75	0.15	0.29
Mg2EDTA-1.0-1	848	9.38E-02	0.94	0.94	10.80	0.15	0.29
Mg2EDTA-1.0-2	848	1.03E-01	0.94	0.94	10.72	0.15	0.29
Mg2EDTA-2.0-1	848	1.06E-01	1.87	1.87	10.78	0.15	0.29
Mg2EDTA-2.0-2	848	1.01E-01	1.87	1.87	10.72	0.15	0.29
Mg2EDTA-3.0-1	848	9.62E-02	2.80	2.80	10.83	0.15	0.29
Mg2EDTA-3.0-2	848	9.24E-02	2.80	2.80	10.77	0.15	0.29
Mg2EDTA-4.0-1	848	9.03E-02	3.74	3.74	11.01	0.15	0.29
Mg2EDTA-4.0-2	848	9.27E-02	3.74	3.74	10.83	0.15	0.29
Mg2EDTA-5.0-1	848	9.65E-02	4.67	4.67	10.71	0.15	0.29
Mg2EDTA-5.0-2	848	9.69E-02	4.67	4.67	11.01	0.15	0.29
Mg2EDTA-0.01-1	905	8.13E-02	0.01	0.01	10.61	0.18	0.37
Mg2EDTA-0.01-2	905	9.89E-02	0.01	0.01	10.56	0.15	0.29
Mg2EDTA-0.1-1	905	1.02E-01	0.09	0.09	10.75	0.15	0.29
Mg2EDTA-0.1-2	905	1.01E-01	0.09	0.09	10.62	0.15	0.29
Mg2EDTA-1.0-1	905	1.00E-01	0.94	0.94	10.68	0.15	0.29
Mg2EDTA-1.0-2	905	9.55E-02	0.94	0.94	10.67	0.15	0.29
Mg2EDTA-2.0-1	905	1.13E-01	1.87	1.87	10.71	0.15	0.29
Mg2EDTA-2.0-2	905	8.88E-02	1.87	1.87	10.66	0.15	0.29
Mg2EDTA-3.0-1	905	1.01E-01	2.80	2.80	10.77	0.15	0.29
Mg2EDTA-3.0-2	905	9.18E-02	2.80	2.80	10.64	0.15	0.29
Mg2EDTA-4.0-1	905	9.88E-02	3.74	3.74	10.92	0.15	0.29
Mg2EDTA-4.0-2	905	9.03E-02	3.74	3.74	10.75	0.15	0.29
Mg2EDTA-5.0-1	905	9.75E-02	4.67	4.67	10.62	0.15	0.29
Mg2EDTA-5.0-2	905	9.96E-02	4.67	4.67	10.96	0.15	0.29
Mg2EDTA-0.01-1	951	7.68E-02	0.01	0.01	10.56	0.18	0.37
Mg2EDTA-0.01-2	951	1.14E-01	0.01	0.01	10.52	0.15	0.29
Mg2EDTA-0.1-1	951	1.03E-01	0.09	0.09	10.66	0.15	0.29
Mg2EDTA-0.1-2	951	9.36E-02	0.09	0.09	10.56	0.15	0.29
Mg2EDTA-1.0-1	951	9.16E-02	0.94	0.94	10.61	0.15	0.29

Mg2EDTA-1.0-2	951	9.82E-02	0.94	0.94	10.58	0.15	0.29
Mg2EDTA-2.0-1	951	1.04E-01	1.87	1.87	10.60	0.15	0.29
Mg2EDTA-2.0-2	951	1.02E-01	1.87	1.87	10.55	0.15	0.29
Mg2EDTA-3.0-1	951	9.35E-02	2.80	2.80	10.64	0.15	0.29
Mg2EDTA-3.0-2	951	8.86E-02	2.80	2.80	10.47	0.15	0.29
Mg2EDTA-4.0-1	951	8.48E-02	3.74	3.74	10.77	0.15	0.29
Mg2EDTA-4.0-2	951	9.34E-02	3.74	3.74	10.63	0.15	0.29
Mg2EDTA-5.0-1	951	9.68E-02	4.67	4.67	10.45	0.15	0.29
Mg2EDTA-5.0-2	951	9.20E-02	4.67	4.67	10.80	0.15	0.29
Mg2EDTA-0.01-1	1000	8.10E-02	0.01	0.01	10.55	0.18	0.37
Mg2EDTA-0.01-2	1000	1.11E-01	0.01	0.01	10.47	0.15	0.29
Mg2EDTA-0.1-1	1000	1.02E-01	0.09	0.09	10.62	0.15	0.29
Mg2EDTA-0.1-2	1000	9.92E-02	0.09	0.09	10.52	0.15	0.29
Mg2EDTA-1.0-1	1000	9.30E-02	0.94	0.94	10.59	0.15	0.29
Mg2EDTA-1.0-2	1000	1.03E-01	0.94	0.94	10.56	0.15	0.29
Mg2EDTA-2.0-1	1000	1.04E-01	1.87	1.87	10.55	0.15	0.29
Mg2EDTA-2.0-2	1000	1.04E-01	1.87	1.87	10.52	0.15	0.29
Mg2EDTA-3.0-1	1000	9.21E-02	2.80	2.80	10.62	0.15	0.29
Mg2EDTA-3.0-2	1000	9.64E-02	2.80	2.80	10.45	0.15	0.29
Mg2EDTA-4.0-1	1000	9.60E-02	3.74	3.74	10.73	0.15	0.29
Mg2EDTA-4.0-2	1000	9.19E-02	3.74	3.74	10.59	0.15	0.29
Mg2EDTA-5.0-1	1000	9.58E-02	4.67	4.67	10.43	0.15	0.29
Mg2EDTA-5.0-2	1000	8.87E-02	4.67	4.67	10.80	0.15	0.29
Mg2EDTA-0.01-1	1056	7.53E-02	0.01	0.01	10.58	0.18	0.37
Mg2EDTA-0.01-2	1056	1.11E-01	0.01	0.01	10.50	0.15	0.29
Mg2EDTA-0.1-1	1056	1.06E-01	0.09	0.09	10.66	0.15	0.29
Mg2EDTA-0.1-2	1056	1.01E-01	0.09	0.09	10.54	0.15	0.29
Mg2EDTA-1.0-1	1056	8.97E-02	0.94	0.94	10.63	0.15	0.29
Mg2EDTA-1.0-2	1056	9.92E-02	0.94	0.94	10.61	0.15	0.29
Mg2EDTA-2.0-1	1056	1.02E-01	1.87	1.87	10.60	0.15	0.29
Mg2EDTA-2.0-2	1056	9.97E-02	1.87	1.87	10.56	0.15	0.29
Mg2EDTA-3.0-1	1056	9.45E-02	2.80	2.80	10.63	0.15	0.29
Mg2EDTA-3.0-2	1056	9.23E-02	2.80	2.80	10.45	0.15	0.29
Mg2EDTA-4.0-1	1056	8.90E-02	3.74	3.74	10.73	0.15	0.29
Mg2EDTA-4.0-2	1056	9.38E-02	3.74	3.74	10.61	0.15	0.29
Mg2EDTA-5.0-1	1056	9.16E-02	4.67	4.67	10.80	0.15	0.29
Mg2EDTA-5.0-2	1056	9.77E-02	4.67	4.67	10.46	0.15	0.29
Mg2EDTA-0.01-2	1213	1.10E-01	0.01	0.01	10.51	0.15	0.29

Mg2EDTA-0.1-1	1213	1.04E-01	0.09	0.09	10.66	0.15	0.29
Mg2EDTA-0.1-2	1213	9.92E-02	0.09	0.09	10.54	0.15	0.29
Mg2EDTA-1.0-1	1213	9.12E-02	0.94	0.94	10.64	0.15	0.29
Mg2EDTA-1.0-2	1213	9.95E-02	0.94	0.94	10.62	0.15	0.29
Mg2EDTA-2.0-1	1213	1.03E-01	1.87	1.87	10.60	0.15	0.29
Mg2EDTA-2.0-2	1213	9.90E-02	1.87	1.87	10.55	0.15	0.29
Mg2EDTA-3.0-1	1213	9.40E-02	2.80	2.80	10.60	0.15	0.29
Mg2EDTA-3.0-2	1213	8.63E-02	2.80	2.80	10.38	0.15	0.29
Mg2EDTA-4.0-1	1213	9.08E-02	3.74	3.74	10.68	0.15	0.29
Mg2EDTA-4.0-2	1213	8.98E-02	3.74	3.74	10.60	0.15	0.29
Mg2EDTA-5.0-1	1213	9.88E-02	4.67	4.67	10.45	0.15	0.29
Mg2EDTA-5.0-2	1213	9.33E-02	4.67	4.67	10.79	0.15	0.29
Mg2EDTA-0.01-1	1302	7.97E-02	0.01	0.01	10.52	0.18	0.37
Mg2EDTA-0.01-2	1302	1.15E-01	0.01	0.01	10.43	0.15	0.29
Mg2EDTA-0.1-1	1302	1.07E-01	0.09	0.09	10.57	0.15	0.29
Mg2EDTA-0.1-2	1302	9.96E-02	0.09	0.09	10.45	0.15	0.29
Mg2EDTA-1.0-1	1302	9.41E-02	0.94	0.94	10.56	0.15	0.29
Mg2EDTA-1.0-2	1302	1.03E-01	0.94	0.94	10.54	0.15	0.29
Mg2EDTA-2.0-1	1302	1.06E-01	1.87	1.87	10.51	0.15	0.29
Mg2EDTA-2.0-2	1302	1.03E-01	1.87	1.87	10.48	0.15	0.29
Mg2EDTA-3.0-1	1302	9.70E-02	2.80	2.80	10.52	0.15	0.29
Mg2EDTA-3.0-2	1302	9.42E-02	2.80	2.80	10.28	0.15	0.29
Mg2EDTA-4.0-1	1302	9.72E-02	3.74	3.74	10.60	0.15	0.29
Mg2EDTA-4.0-2	1302	9.48E-02	3.74	3.74	10.51	0.15	0.29
Mg2EDTA-5.0-1	1302	9.78E-02	4.67	4.67	10.39	0.15	0.29
Mg2EDTA-5.0-2	1302	9.49E-02	4.67	4.67	10.69	0.15	0.29
Mg2EDTA-0.01-1	1345	7.77E-02	0.01	0.01	10.50	0.18	0.37
Mg2EDTA-0.01-2	1345	1.07E-01	0.01	0.01	10.43	0.15	0.29
Mg2EDTA-0.1-1	1345	1.03E-01	0.09	0.09	10.53	0.15	0.29
Mg2EDTA-0.1-2	1345	1.01E-01	0.09	0.09	10.43	0.15	0.29
Mg2EDTA-1.0-1	1345	9.19E-02	0.94	0.94	10.54	0.15	0.29
Mg2EDTA-1.0-2	1345	9.61E-02	0.94	0.94	10.51	0.15	0.29
Mg2EDTA-2.0-1	1345	1.02E-01	1.87	1.87	10.49	0.15	0.29
Mg2EDTA-2.0-2	1345	9.83E-02	1.87	1.87	10.44	0.15	0.29
Mg2EDTA-3.0-1	1345	9.98E-02	2.80	2.80	10.48	0.15	0.29
Mg2EDTA-3.0-2	1345	9.63E-02	2.80	2.80	10.24	0.15	0.29
Mg2EDTA-4.0-1	1345	9.28E-02	3.74	3.74	10.55	0.15	0.29
Mg2EDTA-4.0-2	1345	9.32E-02	3.74	3.74	10.46	0.15	0.29
Mg2EDTA-5.0-1	1345	1.00E-01	4.67	4.67	10.35	0.15	0.29

Mg2EDTA-5.0-2	1345	9.19E-02	4.67	4.67	10.64	0.15	0.29

*Notice that the experimental data presented in the report were up to 1,056 days. The experimental data after 1,056 days have been reviewed, and they are in Kirkes et al. (2014).

[A] pH readings obtained by using a pH electrode were first converted to hydrogen ion concentrations on molar scale (pcH) by applying correction factors from Rai et al. (1997), and then converted to hydrogen ion concentrations on molal scale (pmH) using the equation of Xiong et al. (2010) based on molality/molarity ratios listed under the tab "MolalityToMolarityRatios" in the Spreadsheet AR_AP154_Tasks18-19_Modeling.xls.

[B] Notice that the concentrations of Na, Mg, Cl and EDTA of the prepared solutions were used in this AR, this is because they are major components of the supporting solutions so that their analyses require very high dilutions, resulting in relatively large uncertainties.

Table 3. Experimental results concerning solubility of PbO(cr) in $MgCl_2$ solutions produced at SNL at 22.5 ± 1.5 °C*.

Experimental number	Day	ΣPb, $mol \cdot kg^{-1}$	ΣMg, $mol \cdot kg^{-1}$	ΣCl, $mol \cdot kg^{-1}$	pmH [A]	ΣEDTA, $mol \cdot kg^{-1}$
PbO-0.01ED-1	328	3.58E-02	8.00E-03	0.0160	11.70	0.0418
PbO-0.01ED-2	328	3.52E-02	8.00E-03	0.0160	11.64	0.0418
PbO-0.1ED-1	328	3.44E-02	0.0800	0.160	9.61	0.0418
PbO-0.1ED-2	328	3.39E-02	0.0800	0.160	9.62	0.0418
PbO-1.0ED-1	328	2.50E-02	0.800	1.60	9.25	0.0418
PbO-1.0ED-2	328	2.31E-02	0.800	1.60	9.25	0.0418
PbO-1.5ED-1	328	1.95E-02	1.20	2.40	9.20	0.0418
PbO-1.5ED-2	328	1.89E-02	1.20	2.40	9.20	0.0418
PbO-2.0ED-1	328	1.59E-02	1.60	3.20	9.16	0.0418
PbO-2.0ED-2	328	1.69E-02	1.60	3.20	9.15	0.0418
PbO-2.5ED-1	328	1.63E-02	2.00	4.00	9.11	0.0418
PbO-2.5ED-2	328	1.58E-02	2.00	4.00	9.10	0.0418
PbO-0.01ED-1	407	3.61E-02	8.00E-03	0.0160	11.67	0.0418
PbO-0.01ED-2	407	3.58E-02	8.00E-03	0.0160	11.65	0.0418
PbO-0.1ED-1	407	3.36E-02	0.0800	0.160	9.59	0.0418
PbO-0.1ED-2	407	3.50E-02	0.0800	0.160	9.64	0.0418
PbO-1.0ED-1	407	3.15E-02	0.800	1.60	9.19	0.0418
PbO-1.0ED-2	407	3.19E-02	0.800	1.60	9.16	0.0418
PbO-1.5ED-1	407	3.13E-02	1.20	2.40	9.09	0.0418
PbO-1.5ED-2	407	3.10E-02	1.20	2.40	9.16	0.0418
PbO-2.0ED-1	407	2.97E-02	1.60	3.20	9.03	0.0418
PbO-2.0ED-2	407	3.01E-02	1.60	3.20	9.05	0.0418
PbO-2.5ED-1	407	2.73E-02	2.00	4.00	8.98	0.0418
PbO-2.5ED-2	407	3.08E-02	2.00	4.00	8.97	0.0418
PbO-0.01ED-1	937	4.14E-02	8.00E-03	0.0160	11.72	0.0418
PbO-0.01ED-2	937	3.92E-02	8.00E-03	0.0160	11.70	0.0418
PbO-0.1ED-1	937	3.81E-02	0.0800	0.160	9.59	0.0418
PbO-0.1ED-2	937	3.91E-02	0.0800	0.160	9.58	0.0418
PbO-1.0ED-1	937	3.80E-02	0.800	1.60	9.20	0.0418
PbO-1.0ED-2	937	3.72E-02	0.800	1.60	9.19	0.0418

PbO-1.5ED-1	937	3.73E-02	1.20	2.40	9.16	0.0418
PbO-1.5ED-2	937	3.91E-02	1.20	2.40	9.17	0.0418
PbO-2.0ED-1	937	3.47E-02	1.60	3.20	9.09	0.0418
PbO-2.0ED-2	937	4.14E-02	1.60	3.20	9.12	0.0418
PbO-2.5ED-1	937	3.71E-02	2.00	4.00	8.95	0.0418
PbO-2.5ED-2	937	3.70E-02	2.00	4.00	8.95	0.0418
PbO-0.01ED-1	986	4.01E-02	8.00E-03	0.0160	11.66	0.0418
PbO-0.01ED-2	986	3.97E-02	8.00E-03	0.0160	11.63	0.0418
PbO-0.1ED-1	986	3.89E-02	0.0800	0.160	9.51	0.0418
PbO-0.1ED-2	986	3.96E-02	0.0800	0.160	9.47	0.0418
PbO-1.0ED-1	986	3.79E-02	0.800	1.60	9.16	0.0418
PbO-1.0ED-2	986	3.73E-02	0.800	1.60	9.20	0.0418
PbO-1.5ED-1	986	3.76E-02	1.20	2.40	9.15	0.0418
PbO-1.5ED-2	986	3.74E-02	1.20	2.40	9.16	0.0418
PbO-2.0ED-1	986	3.71E-02	1.60	3.20	9.12	0.0418
PbO-2.0ED-2	986	3.64E-02	1.60	3.20	9.12	0.0418
PbO-2.5ED-1	986	3.76E-02	2.00	4.00	8.96	0.0418
PbO-2.5ED-2	986	3.79E-02	2.00	4.00	8.97	0.0418
PbO-0.01ED-1	1035	4.06E-02	8.00E-03	0.0160	11.77	0.0418
PbO-0.01ED-2	1035	4.14E-02	8.00E-03	0.0160	11.76	0.0418
PbO-0.1ED-1	1035	4.09E-02	0.0800	0.160	9.60	0.0418
PbO-0.1ED-2	1035	3.97E-02	0.0800	0.160	9.62	0.0418
PbO-1.0ED-1	1035	4.29E-02	0.800	1.60	9.21	0.0418
PbO-1.0ED-2	1035	4.07E-02	0.800	1.60	9.14	0.0418
PbO-1.5ED-1	1035	4.09E-02	1.20	2.40	9.15	0.0418
PbO-1.5ED-2	1035	4.11E-02	1.20	2.40	9.18	0.0418
PbO-2.0ED-1	1035	3.98E-02	1.60	3.20	9.03	0.0418
PbO-2.0ED-2	1035	3.94E-02	1.60	3.20	9.16	0.0418
PbO-2.5ED-1	1035	3.82E-02	2.00	4.00	9.04	0.0418
PbO-2.5ED-2	1035	3.79E-02	2.00	4.00	9.05	0.0418
PbO-0.01ED-1	1084	4.01E-02	8.00E-03	0.0160	11.70	0.0418
PbO-0.01ED-2	1084	3.91E-02	8.00E-03	0.0160	11.70	0.0418
PbO-0.1ED-1	1084	3.96E-02	0.0800	0.160	9.56	0.0418
PbO-0.1ED-2	1084	3.96E-02	0.0800	0.160	9.55	0.0418

PbO-1.0ED-1	1084	3.84E-02	0.800	1.60	9.16	0.0418
PbO-1.0ED-2	1084	3.40E-02	0.800	1.60	9.19	0.0418
PbO-1.5ED-1	1084	3.78E-02	1.20	2.40	9.15	0.0418
PbO-1.5ED-2	1084	3.75E-02	1.20	2.40	9.16	0.0418
PbO-2.0ED-1	1084	3.80E-02	1.60	3.20	9.09	0.0418
PbO-2.0ED-2	1084	3.74E-02	1.60	3.20	9.10	0.0418
PbO-2.5ED-1	1084	3.73E-02	2.00	4.00	8.93	0.0418
PbO-2.5ED-2	1084	3.71E-02	2.00	4.00	8.93	0.0418
PbO-0.01ED-1	1236	3.99E-02	8.00E-03	0.0160	11.75	0.0418
PbO-0.01ED-2	1236	3.94E-02	8.00E-03	0.0160	11.74	0.0418
PbO-0.1ED-1	1236	3.88E-02	0.0800	0.160	9.62	0.0418
PbO-0.1ED-2	1236	3.90E-02	0.0800	0.160	9.58	0.0418
PbO-1.0ED-1	1236	3.64E-02	0.800	1.60	9.27	0.0418
PbO-1.0ED-2	1236	3.79E-02	0.800	1.60	9.28	0.0418
PbO-1.5ED-1	1236	3.67E-02	1.20	2.40	9.23	0.0418
PbO-1.5ED-2	1236	3.68E-02	1.20	2.40	9.22	0.0418
PbO-2.0ED-1	1236	3.67E-02	1.60	3.20	9.18	0.0418
PbO-2.0ED-2	1236	4.02E-02	1.60	3.20	9.17	0.0418
PbO-2.5ED-1	1236	3.61E-02	2.00	4.00	8.99	0.0418
PbO-2.5ED-2	1236	3.59E-02	2.00	4.00	8.99	0.0418
PbO-0.01ED-1	1344	3.99E-02	8.00E-03	0.0160	11.71	0.0418
PbO-0.01ED-2	1344	3.99E-02	8.00E-03	0.0160	11.70	0.0418
PbO-0.1ED-1	1344	3.94E-02	0.0800	0.160	9.55	0.0418
PbO-0.1ED-2	1344	3.93E-02	0.0800	0.160	9.56	0.0418
PbO-1.0ED-1	1344	3.67E-02	0.800	1.60	9.22	0.0418
PbO-1.0ED-2	1344	3.71E-02	0.800	1.60	9.22	0.0418
PbO-1.5ED-1	1344	3.63E-02	1.20	2.40	9.17	0.0418
PbO-1.5ED-2	1344	3.61E-02	1.20	2.40	9.17	0.0418
PbO-2.0ED-1	1344	3.55E-02	1.60	3.20	9.12	0.0418
PbO-2.0ED-2	1344	3.55E-02	1.60	3.20	9.11	0.0418
PbO-2.5ED-1	1344	3.68E-02	2.00	4.00	8.94	0.0418
PbO-2.5ED-2	1344	3.70E-02	2.00	4.00	8.94	0.0418

* Notice that the experimental data presented in the report were up to 1,084 days. The experimental data after 1,084 days have been reviewed, and they are Kirkes et al. (2014).

[A] pH readings obtained by using a pH electrode were first converted to hydrogen ion concentrations on molar scale (pcH) by applying correction factors (Hansen, 2001), and then converted to hydrogen ion concentrations on molal scale (pmH) using the equation of Xiong et al. (2010) based on molality/molarity ratios listed under the tab "MolalityToMolarityRatios" in the Spreadsheet AR_AP154_Tasks18-19_Modeling.xls.

Table 4. Equilibrium constants at infinite dilution at 25°C and 1 bar for the Na^+—Mg^{2+}—Pb^{2+}—Cl^-—$EDTA^{4-}$ system

Reactions	log K^o_{s2}, log β^o_1	Reference and Remarks
$PbO(cr) + 2H^+ = Pb^{2+} + H_2O$	12.59	ymp.R2/ymp.R0
$Pb^{2+} + EDTA^{4-} = PbEDTA^{2-}$	20.42 ± 0.21 (2σ)	Based the value of 18.30 from Andregg (1977) at 0.1 M extrapolated to infinite dilution using the Davies equation (i.e., Eq. 5).
$Pb^{2+} + EDTA^{4-} = PbEDTA^{2-}$	20.01 ± 0.20 (2σ)	Based the value of 17.42 from Uhler and Helz (1984) at 0.16 M extrapolated to infinite dilution using the Davies equation (i.e., Eq. 5).
$Pb^{2+} + EDTA^{4-} = PbEDTA^{2-}$	20.00 ± 0.20 (2σ)	This work*, based on modeling solubility data in NaCl and $MgCl_2$ solutions.

*The parameter obtained corresponds to Iteration 44 (please see Results_PD_08-21-14.txt and Results_data0P18_08-25-14_XYL.txt).

Table 5. Pitzer interaction parameters at 25°C and 1 bar for the Na^+—Mg^{2+}—Pb^{2+}—Cl^-—$EDTA^{4-}$ system

Pitzer Binary Interaction Parameters					
Species *i*	Species *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	Reference
Na^+	$PbEDTA^{2-}$	0.65	1.74	0.065	This study*
Mg^{2+}	$PbEDTA^{2-}$	1.84	3.27	-0.15	This study*

*The parameter obtained corresponds to Iteration 44 (please see Results_PD_08-21-14.txt, and Results_data0P18_08-25-14_XYL.txt).

Table 6. 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 AR_AP154_Tasks18-19_Modeling.xls	In zip file AP154_Tasks18-19_DataPackage.zip, library LIBAP154_FILES
EQ3/6 DB DATA0.p18	In zip file AP154_Tasks18-19_DataPackage.zip, library LIBAP154_FILES
EQ3/6 I/O files: EDNa.3i through EDNa-75.3i PbEB-1.3i through PbEB-75.3i	In zip file AP154_Tasks18-19_DataPackage.zip, library LIBAP154_FILES
Python input script for modeling: PbEDTA_NaCl_MgCl2_logK_subroutine_4parameters.py	In zip file AP154_Tasks18-19_DataPackage.zip, library LIBAP154_FILES
Modeling Results: Results_PD_08-21-14.txt; Results_data0P18_08-25-14_XYL.txt Results_logK=20.42.txt Results_logK=20.20.txt Results_logK=20.10.txt Results_logK=20.0009.txt	In zip file AP154_Tasks18-19_DataPackage.zip, library LIBAP154_FILES

* The path for where the files are located:
/nfs/data/CVSLIB/WIPP_EXTERNAL/ap154_files/Files.

3 RESULTS

Tables 4 and 5 provide the log K^{o}_{s2}, and Pitzer parameter associated with log β^{o}_{1} in the Na^{+}—Mg^{2+}—Pb^{2+}—Cl^{-}—$EDTA^{4-}$ system derived in this study.

The Pitzer parameters evaluated by this study are similar to literature values for the similar interactions in terms of magnitude. For example, $\beta^{(0)}$ for Na^{+}—$PbEDTA^{2-}$ is 0.25, in comparison of 0.4733 and 0.2134 for Na^{+}—NpO_2HEDTA^{2-} and Na^{+}—$MgEDTA^{2-}$ in data0.fm1, respectively. The C^{ϕ} for Na^{+}—$PbEDTA^{2-}$ is 0.0525, in comparison of 0.00869 and 0.142 for Na^{+}—$MgEDTA^{2-}$ and Na^{+}—$NpO_2Citrate^{2-}$ in data0.fm1, respectively. The $\beta^{(0)}$ for Mg^{2+}—$PbEDTA^{2-}$ is 0.85, in comparison of -1.42258 from Yin et al. (2007) for the Mg^{2+}—$B_4O_2(OH)_4^{2-}$

interaction. The C^{ϕ} for Mg^{2+}—$PbEDTA^{2-}$ is 0.1, in comparison of 0.025 for the Mg^{2+}—SO_4^{2-} interaction in data0.fm1.

4 CONCLUSIONS

In this analysis report, the Pitzer parameter associated with log β_1^o for $PbEDTA^{2-}$ in the Na^+—Mg^{2+}—Pb^{2+}—Cl^-—$EDTA^{4-}$ system are obtained. With these parameters, the interactions of lead as radiation shielding material with $EDTA^{4-}$ in the brines can be accurately modeled, and would have a direct impact on PA.

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