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Sandia National Laboratories
Waste Isolation Pilot Plant

Experimental and Thermodynamic Modeling Solubility of Cerussite, $PbCO_3(cr)$, in the Carbonate System to High Ionic Strengths, Revision 1, Supersedes ERMS 561917

Work Carried Out under Tasks 14 and 15 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.

Carbonate is an important inorganic ligand 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. When lead is corroded under anoxic conditions in carbonate-containing brines, lead carbonate, cerussite ($PbCO_3$(cr)), is expected to form. Therefore, the accurate knowledge of solubilities of cerussite 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 cerussite in $NaHCO_3$ + NaCl and mixtures of $NaHCO_3$ and Na_2CO_3 solutions.

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 14 and 15 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.

In order to be consistent with the parameters related to Pb hydroxyl species recently obtained under AP 155, the AR of Xiong (2014) is slightly revised. In Revision 0, the lead hydroxyl species, $PbOH^+$, $Pb(OH)_2$(aq), and $Pb(OH)_3^-$, were not concluded. Under AP 155, these lead hydroxyl species are evaluated. Although it has been *correctly* assumed in Revision 0 that the contributions from lead hydroxyl species are insignificant (i.e., less than 1%) in the experimental systems, the AR is revised for inclusion of lead hydroxyl species for the sake of consistency.

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
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^+–Pb^{2+}–Cl^-–HCO_3^-–CO_3^{2-} system based on solubility data of cerussite in $NaHCO_3$ and Na_2CO_3 solutions produced at SNL (Jang, Xiong, Kim, and Nemer, 2012) under TP 08-02. Tables 2 and 3 list experimental data in $NaHCO_3$ with 0.15–0.3 mol kg^{-1} NaCl, and in the mixtures of $NaHCO_3$ + Na_2CO_3 solutions from the above report, respectively.

The dissolution reaction for $PbCO_3$(cr) can be expressed as,

$$PbCO_3(cr) = Pb^{2+} + CO_3^{2-} \quad (1)$$

The corresponding solubility product constant of $PbCO_3$(cr) at infinite dilution can be cast as follows,

$$K_s^o = \frac{a_{Pb^{2+}} \times a_{CO_3^{2-}}}{a_{PbCO_3(cr)}} \quad (2)$$

In this analysis, the aqueous lead species included are Pb^{2+}, $PbCl^+$, $PbCl_2$(aq), $PbCl_3^-$, $PbCO_3$(aq), $Pb(CO_3)_2^{2-}$, and $Pb(CO_3)Cl^-$. 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 lead carbonate species, $PbCO_3$(aq), $Pb(CO_3)_2^{2-}$, and $Pb(CO_3)Cl^-$, are recommended by Powell et al. (2009) and Woosley and Millero (2013). In addition, Powell et al. (2009) mentioned the complex, $PbHCO_3^-$. However, the strength of this complex is very weak in comparison with $PbCO_3$(aq), $Pb(CO_3)_2^{2-}$, and $PbCO_3Cl^-$. Therefore, it is not included in the model developed in this analysis.

It should be mentioned that the studies published after our TP have indicated that chloride ion (Cl^-) forms a relatively strong ternary complex with CO_3^{2-} and Pb^{2+} (Woosley and Millero, 2013), i.e., $Pb(CO_3)Cl^-$, in comparison with the binary complex $PbCl^+$. The log β_{11} for $Pb(CO_3)Cl^-$ and log β_1 for $PbCl^+$ are 7.23 (Woosley and Millero, 2013) and 1.48 (Millero and Byrne, 1984), respectively. The same is true with the strengths of $PbCO_3$(aq) and $Pb(CO_3)_2^{2-}$ in comparison with $PbCl^+$. The log β_1 for $PbCO_3$(aq) and log β_2 for $Pb(CO_3)_2^{2-}$ are 6.87 (Woosley and Millero, 2013) and 10.41 (Easley and Byrne, 2011), respectively. Therefore, our experimental data are used to model the interaction of the matrixes with $Pb(CO_3)Cl^-$, $PbCO_3$(aq), and $Pb(CO_3)_2^{2-}$, instead of $PbCl^+$. This is based on the initial assessment which indicated that the contributions from the sum of lead chloride complexes including $PbCl^+$, $PbCl_2$(aq) and $PbCl_3^-$, to the total lead concentrations are less than 0.1%. This can be confirmed by checking output files in pmh-*.3o series in which chloride is present included with this AR.

The formation reaction for $PbCO_3$(aq) is written as,

$$Pb^{2+} + CO_3^{2-} = PbCO_3(aq) \quad (3)$$

The corresponding cumulative formation constant at infinite dilution is,

$$\beta_1^0 = \frac{a_{PbCO_3(aq)}}{a_{Pb^{2+}} \times a_{CO_3^{2-}}} \quad (4)$$

Similarly, the cumulative formation reaction for $Pb(CO_3)_2^{2-}$ can be written as,

$$Pb^{2+} + 2CO_3^{2-} = Pb(CO_3)_2^{2-} \quad (5)$$

The corresponding cumulative formation constant at infinite dilution should be,

$$\beta_2^0 = \frac{a_{Pb(CO_3)_2^{2-}}}{a_{Pb^{2+}} \times (a_{CO_3^{2-}})^2} \quad (6)$$

The cumulative formation reaction for the $Pb(CO_3)Cl^-$ complex as follows,

$$Pb^{2+} + CO_3^{2-} + Cl^- = Pb(CO_3)Cl^- \quad (7)$$

The corresponding cumulative formation constant for this ternary complex at infinite dilution is as follows,

$$\beta_{11}^0 = \frac{a_{Pb(CO_3)Cl^-}}{a_{Pb^{2+}} \times a_{CO_3^{2-}} \times a_{Cl^-}} \quad (8)$$

In this analysis report, the above cumulative formation constants are taken from the literature (Easley and Byrne, 2011; Woosley and Millero, 2013), and associated Pitzer parameters for the interactions of $PbCO_3(aq)$ with Cl^- and Na^+ are from Woosley and Millero (2013) (Table 4).

Using experimental solubility data of $PbCO_3(cr)$ in $NaHCO_3$ solutions with 0.15–0.3 mol•kg^{-1} NaCl, and in the mixtures of $NaHCO_3 + Na_2CO_3$ from this work, log K_s^o for Reaction (1), and the Pitzer parameters associated with $Pb(CO_3)Cl^-$ and $Pb(CO_3)_2^{2-}$ are modeled using EQ3/6 Version 8.0a (Tables 4 and 5) with the Python script (Kirchner, 2012). Notice that the Pitzer parameters related to $PbCO_3(aq)$ are taken from Woosley and Millero (2013) (Table 5).

In the modeling, the experimental data in $NaHCO_3$ solutions with 0.15–0.3 mol•kg^{-1} NaCl are employed to generate EQ3 files from pmH-1.3i through pmH-70.3i. Similarly, the experimental data in the mixtures of $NaHCO_3 + Na_2CO_3$ are used to produce EQ3 input files from buff-1.3i through buff-80.3i. Notice that there are more than 80 data points in the experimental set in the mixtures of $NaHCO_3 + Na_2CO_3$. However, only the first 80 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 $NaHCO_3$ solutions with 0.15–0.3 $mol \cdot kg^{-1}$ NaCl (70 input files in subtotal) are combined with those from the experimental set in the mixtures of $NaHCO_3 + Na_2CO_3$ (80 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. The model-predicted solubility curve was compared with the experimental data (see Excel spreadsheet "AR_AP154_Tasks14-15_Modeling.xls"). A plot showing such comparisons is shown in Figure 1. The solubility curve for $PbCO_3$(cr) was established using EQ3/6 files VerEQ3-1.3i through VerEQ3-5.3i located in the zip file "AP154_Tasks14-15_DataPackage.zip" (Table 6) using the database DATA0.OX3 (Table 6).

In Figure 1, experimental data in $NaHCO_3$ solutions with 0.15–0.3 $mol \cdot kg^{-1}$ NaCl are compared with the model-predicted values. There are two solubility curves predicted by the model in Figure 1. In one solubility curve, the theta parameters for HCO_3^-—$Pb(CO_3)_2^{2-}$ and CO_3^{2-}—$Pb(CO_3)_2^{2-}$ are set to zero. The associated output files are located in the folder "Zero theta parameters". In the other solubility curve, the theta parameters for HCO_3^-—$Pb(CO_3)_2^{2-}$ and CO_3^{2-}—$Pb(CO_3)_2^{2-}$ are those listed in Table 5. The associated EQ3 output files are located in the folder "Non-zero theta parameters". Similarly, experimental data in the mixtures of $NaHCO_3 + Na_2CO_3$ are also compared with the model-predicted values in Figure 2. There are also two solubility curves predicted by the model in Figure 2. The associated EQ3 output files are located in folders "NaHCO3-Na2CO3_Zero theta parameters" and "NaHCO3-Na2CO3_Non-zero theta parameters", respectively. Figures 1 and 2 demonstrate that the model without the theta parameters for HCO_3^-—$Pb(CO_3)_2^{2-}$ and CO_3^{2-}—$Pb(CO_3)_2^{2-}$ performs better than the model with the theta parameters for HCO_3^-—$Pb(CO_3)_2^{2-}$ and CO_3^{2-}—$Pb(CO_3)_2^{2-}$. Therefore, in the light of the comparisons, the theta parameters for HCO_3^-—$Pb(CO_3)_2^{2-}$ and CO_3^{2-}—$Pb(CO_3)_2^{2-}$ will not enter the final database.

Table 2. Experimental results concerning solubility of $PbCO_3$(cr) in $NaHCO_3$ solutions with 0.15–0.3 mol•kg^{-1} NaCl produced at SNL at 22.5 ± 1.5 °C (from Jang, Xiong, Kim, and Nemer, 2012)*.

Experimental number	day	ΣPb, mol•kg^{-1}	ΣNa, mol•kg^{-1}	ΣCl, mol•kg^{-1}	pmH [A]	ΣCO_3, mol•kg^{-1}
PbCO3-0.01/0.15-1	741	1.12E-06	0.1586	0.15	9.10	8.60E-03
PbCO3-0.01/0.15-2	741	7.10E-07	0.1586	0.15	9.37	8.60E-03
PbCO3-0.05/0.15-1	741	2.94E-06	0.193	0.15	9.04	4.30E-02
PbCO3-0.05/0.15-2	741	2.94E-06	0.193	0.15	9.03	4.30E-02
PbCO3-0.5/0.15-1	741	2.58E-05	0.58	0.15	8.82	4.30E-01
PbCO3-0.5/0.15-2	741	2.69E-05	0.58	0.15	8.92	4.30E-01
PbCO3-1.0/0.15-1	741	5.83E-05	1.01	0.15	8.77	8.60E-01
PbCO3-1.0/0.15-2	741	6.04E-05	1.01	0.15	8.70	8.60E-01
PbCO3-1.0/0.30-1	741	6.68E-05	1.16	0.3	8.72	8.60E-01
PbCO3-1.0/0.30-2	741	7.13E-05	1.16	0.3	8.70	8.60E-01
PbCO3-0.01/0.15-1	1020	5.83E-07	0.1586	0.15	8.71	8.60E-03
PbCO3-0.01/0.15-2	1020	3.92E-06	0.1586	0.15	9.17	8.60E-03
PbCO3-0.05/0.15-1	1020	4.96E-06	0.193	0.15	8.94	4.30E-02
PbCO3-0.05/0.15-2	1020	4.73E-06	0.193	0.15	9.09	4.30E-02
PbCO3-0.5/0.15-1	1020	9.64E-05	0.58	0.15	9.68	4.30E-01
PbCO3-0.5/0.15-2	1020	4.48E-05	0.58	0.15	9.08	4.30E-01
PbCO3-1.0/0.15-1	1020	8.90E-05	1.01	0.15	8.96	8.60E-01
PbCO3-1.0/0.15-2	1020	8.11E-05	1.01	0.15	8.87	8.60E-01
PbCO3-1.0/0.30-1	1020	1.25E-04	1.16	0.3	9.06	8.60E-01
PbCO3-1.0/0.30-2	1020	9.16E-05	1.16	0.3	8.90	8.60E-01
PbCO3-0.01/0.15-1	1069	1.59E-06	0.1586	0.15	8.68	8.60E-03
PbCO3-0.01/0.15-2	1069	2.23E-06	0.1586	0.15	9.15	8.60E-03
PbCO3-0.05/0.15-1	1069	5.14E-06	0.193	0.15	8.98	4.30E-02
PbCO3-0.05/0.15-2	1069	5.03E-06	0.193	0.15	9.10	4.30E-02
PbCO3-0.5/0.15-1	1069	7.14E-05	0.58	0.15	9.55	4.30E-01
PbCO3-0.5/0.15-2	1069	4.65E-05	0.58	0.15	9.09	4.30E-01
PbCO3-1.0/0.15-1	1069	9.94E-05	1.01	0.15	8.96	8.60E-01
PbCO3-1.0/0.15-2	1069	9.28E-05	1.01	0.15	8.89	8.60E-01
PbCO3-1.0/0.30-1	1069	1.27E-04	1.16	0.3	9.07	8.60E-01
PbCO3-1.0/0.30-2	1069	1.06E-04	1.16	0.3	8.90	8.60E-01
PbCO3-0.01/0.15-1	1118	5.96E-07	0.1586	0.15	8.57	8.60E-03

PbCO3-0.01/0.15-2	1118	1.31E-06	0.1586	0.15	9.24	8.60E-03
PbCO3-0.05/0.15-1	1118	3.69E-06	0.193	0.15	9.09	4.30E-02
PbCO3-0.05/0.15-2	1118	4.35E-06	0.193	0.15	9.19	4.30E-02
PbCO3-0.5/0.15-1	1118	6.57E-05	0.58	0.15	9.59	4.30E-01
PbCO3-0.5/0.15-2	1118	5.04E-05	0.58	0.15	9.16	4.30E-01
PbCO3-1.0/0.15-1	1118	1.05E-04	1.01	0.15	9.04	8.60E-01
PbCO3-1.0/0.15-2	1118	9.72E-05	1.01	0.15	8.98	8.60E-01
PbCO3-1.0/0.30-1	1118	1.38E-04	1.16	0.3	9.15	8.60E-01
PbCO3-1.0/0.30-2	1118	1.08E-04	1.16	0.3	8.99	8.60E-01
PbCO3-0.01/0.15-1	1167	3.49E-06	0.1586	0.15	8.60	8.60E-03
PbCO3-0.01/0.15-2	1167	1.42E-06	0.1586	0.15	9.14	8.60E-03
PbCO3-0.05/0.15-1	1167	4.02E-06	0.193	0.15	9.01	4.30E-02
PbCO3-0.05/0.15-2	1167	4.44E-06	0.193	0.15	9.11	4.30E-02
PbCO3-0.5/0.15-1	1167	6.24E-05	0.58	0.15	9.49	4.30E-01
PbCO3-0.5/0.15-2	1167	5.04E-05	0.58	0.15	9.09	4.30E-01
PbCO3-1.0/0.15-1	1167	1.09E-04	1.01	0.15	8.97	8.60E-01
PbCO3-1.0/0.15-2	1167	9.89E-05	1.01	0.15	8.92	8.60E-01
PbCO3-1.0/0.30-1	1167	1.13E-04	1.16	0.3	9.08	8.60E-01
PbCO3-1.0/0.30-2	1167	1.43E-04	1.16	0.3	8.93	8.60E-01
PbCO3-0.01/0.15-1	1293	1.11E-06	0.1586	0.15	8.52	8.60E-03
PbCO3-0.01/0.15-2	1293	2.16E-06	0.1586	0.15	9.22	8.60E-03
PbCO3-0.05/0.15-1	1293	6.25E-06	0.193	0.15	9.07	4.30E-02
PbCO3-0.05/0.15-2	1293	6.73E-06	0.193	0.15	9.17	4.30E-02
PbCO3-0.5/0.15-1	1293	7.49E-05	0.58	0.15	9.54	4.30E-01
PbCO3-0.5/0.15-2	1293	5.27E-05	0.58	0.15	9.17	4.30E-01
PbCO3-1.0/0.15-1	1293	1.13E-04	1.01	0.15	9.06	8.60E-01
PbCO3-1.0/0.15-2	1293	9.78E-05	1.01	0.15	9.01	8.60E-01
PbCO3-1.0/0.30-1	1293	1.37E-04	1.16	0.3	9.16	8.60E-01
PbCO3-1.0/0.30-2	1293	1.11E-04	1.16	0.3	9.03	8.60E-01
PbCO3-0.01/0.15-1	1379	1.97E-07	0.1586	0.15	8.50	8.60E-03
PbCO3-0.01/0.15-2	1379	1.87E-06	0.1586	0.15	9.16	8.60E-03
PbCO3-0.05/0.15-1	1379	3.73E-06	0.193	0.15	9.05	4.30E-02
PbCO3-0.05/0.15-2	1379	4.27E-06	0.193	0.15	9.14	4.30E-02
PbCO3-0.5/0.15-1	1379	6.55E-05	0.58	0.15	9.50	4.30E-01
PbCO3-0.5/0.15-2	1379	6.69E-05	0.58	0.15	9.10	4.30E-01
PbCO3-1.0/0.15-1	1379	1.22E-04	1.01	0.15	8.99	8.60E-01
PbCO3-1.0/0.15-2	1379	1.19E-04	1.01	0.15	8.96	8.60E-01
PbCO3-1.0/0.30-1	1379	1.61E-04	1.16	0.3	9.09	8.60E-01

PbCO3-1.0/0.30-2	1379	1.20E-04	1.16	0.3	8.97	8.60E-01
PbCO3-0.01/0.15-1	1461	8.95E-07	0.1586	0.15	8.52	8.60E-03
PbCO3-0.01/0.15-2	1461	1.04E-05	0.1586	0.15	9.15	8.60E-03
PbCO3-0.05/0.15-1	1461	3.65E-06	0.193	0.15	9.04	4.30E-02
PbCO3-0.05/0.15-2	1461	1.44E-05	0.193	0.15	9.12	4.30E-02
PbCO3-0.5/0.15-1	1461	8.17E-05	0.58	0.15	9.14	4.30E-01
PbCO3-0.5/0.15-2	1461	6.25E-05	0.58	0.15	9.12	4.30E-01
PbCO3-1.0/0.15-1	1461	1.53E-04	1.01	0.15	9.01	8.60E-01
PbCO3-1.0/0.15-2	1461	1.02E-04	1.01	0.15	8.98	8.60E-01
PbCO3-1.0/0.30-1	1461	1.32E-04	1.16	0.3	9.11	8.60E-01
PbCO3-1.0/0.30-2	1461	1.43E-04	1.16	0.3	8.98	8.60E-01

*Notice that the experimental data presented in the report were up to 1,167 days. The experimental data after 1,167 days have been reviewed. For the data at 1,293 days, please see WIPP—Solubility—21 page 96; for the data at 1,379 days, please see WIPP—Solubility—27 page 29; for the data at 1,461 days, please see WIPP—Solubility—27 page 54.

[A] pH readings obtained by using a pH electrode were first converted to hydrogen ion concentrations on molar scale (pcH) by applying correction factors (see SP 12-14, Roselle, 2012), 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_Tasks14-15_Modeling.xls.

Table 3. Experimental results concerning solubility of $PbCO_3$(cr) in the mixtures of $NaHCO_3$ and Na_2CO_3 produced at SNL at 22.5 ± 1.5 °C*.

Experimental number	day	ΣPb, mol•kg^{-1}	ΣNa, mol•kg^{-1}	pmH [A]	ΣCO_3, mol•kg^{-1}
PbCO3-Buffer A-1	238	2.21E-05	0.154	9.86	0.100
PbCO3-Buffer A-2	238	2.19E-05	0.154	9.83	0.100
PbCO3-Buffer B-1	238	5.03E-05	0.49	9.79	0.300
PbCO3-Buffer B-2	238	5.20E-05	0.49	9.78	0.300
PbCO3-Buffer C-1	238	1.95E-04	1.34	10.04	0.800
PbCO3-Buffer C-2	238	1.92E-04	1.34	10.04	0.800
PbCO3-Buffer D-1	238	3.80E-04	2.07	10.28	1.200
PbCO3-Buffer D-2	238	3.97E-04	2.07	10.29	1.200
PbCO3-Buffer E-1	238	9.01E-04	3.2	10.65	1.800
PbCO3-Buffer E-2	238	7.88E-04	3.2	10.65	1.800
PbCO3-Buffer F-1	238	6.97E-04	3.58	10.76	2.000
PbCO3-Buffer F-2	238	5.88E-04	3.58	10.79	2.000
PbCO3-Buffer A-1	287	2.33E-05	0.154	9.86	0.100
PbCO3-Buffer A-2	287	2.23E-05	0.154	9.86	0.100
PbCO3-Buffer B-1	287	5.05E-05	0.49	9.84	0.300
PbCO3-Buffer B-2	287	5.19E-05	0.49	9.85	0.300
PbCO3-Buffer C-1	287	1.95E-04	1.34	10.10	0.800
PbCO3-Buffer C-2	287	1.97E-04	1.34	10.11	0.800
PbCO3-Buffer D-1	287	3.82E-04	2.07	10.35	1.200
PbCO3-Buffer D-2	287	3.88E-04	2.07	10.37	1.200
PbCO3-Buffer E-1	287	7.94E-04	3.2	10.73	1.800
PbCO3-Buffer E-2	287	7.94E-04	3.2	10.73	1.800
PbCO3-Buffer F-1	287	8.33E-04	3.58	10.85	2.000
PbCO3-Buffer F-2	287	8.07E-04	3.58	10.85	2.000
PbCO3-Buffer A-1	336	2.40E-05	0.154	9.85	0.100
PbCO3-Buffer A-2	336	2.31E-05	0.154	9.83	0.100
PbCO3-Buffer B-1	336	5.20E-05	0.49	9.82	0.300
PbCO3-Buffer B-2	336	5.25E-05	0.49	9.82	0.300
PbCO3-Buffer C-1	336	2.06E-04	1.34	10.05	0.800
PbCO3-Buffer C-2	336	2.08E-04	1.34	10.06	0.800
PbCO3-Buffer D-1	336	3.95E-04	2.07	10.27	1.200
PbCO3-Buffer D-2	336	4.07E-04	2.07	10.29	1.200
PbCO3-Buffer E-1	336	8.04E-04	3.2	10.64	1.800
PbCO3-Buffer E-2	336	7.91E-04	3.2	10.65	1.800
PbCO3-Buffer F-1	336	8.76E-04	3.58	10.75	2.000

PbCO3-Buffer F-2	336	8.53E-04	3.58	10.76	2.000
PbCO3-Buffer A-1	385	2.24E-05	0.154	9.84	0.100
PbCO3-Buffer A-2	385	2.20E-05	0.154	9.84	0.100
PbCO3-Buffer B-1	385	5.24E-05	0.49	9.84	0.300
PbCO3-Buffer B-2	385	5.15E-05	0.49	9.83	0.300
PbCO3-Buffer C-1	385	2.05E-04	1.34	10.07	0.800
PbCO3-Buffer C-2	385	2.01E-04	1.34	10.07	0.800
PbCO3-Buffer D-1	385	4.05E-04	2.07	10.30	1.200
PbCO3-Buffer D-2	385	4.08E-04	2.07	10.31	1.200
PbCO3-Buffer E-1	385	8.20E-04	3.2	10.66	1.800
PbCO3-Buffer E-2	385	8.46E-04	3.2	10.67	1.800
PbCO3-Buffer F-1	385	8.46E-04	3.58	10.78	2.000
PbCO3-Buffer F-2	385	9.73E-04	3.58	10.80	2.000
PbCO3-Buffer A-1	511	2.09E-05	0.154	9.84	0.100
PbCO3-Buffer A-2	511	2.09E-05	0.154	9.84	0.100
PbCO3-Buffer B-1	511	5.14E-05	0.49	9.85	0.300
PbCO3-Buffer B-2	511	5.06E-05	0.49	9.85	0.300
PbCO3-Buffer C-1	511	1.81E-04	1.34	10.09	0.800
PbCO3-Buffer C-2	511	1.80E-04	1.34	10.09	0.800
PbCO3-Buffer D-1	511	3.65E-04	2.07	10.33	1.200
PbCO3-Buffer D-2	511	3.68E-04	2.07	10.34	1.200
PbCO3-Buffer E-1	511	7.56E-04	3.2	10.70	1.800
PbCO3-Buffer E-2	511	7.48E-04	3.2	10.69	1.800
PbCO3-Buffer F-1	511	8.54E-04	3.58	10.81	2.000
PbCO3-Buffer F-2	511	8.07E-04	3.58	10.82	2.000
PbCO3-Buffer A-1	601	2.17E-05	0.154	9.83	0.100
PbCO3-Buffer A-2	601	2.20E-05	0.154	9.83	0.100
PbCO3-Buffer B-1	601	5.36E-05	0.49	9.84	0.300
PbCO3-Buffer B-2	601	5.21E-05	0.49	9.83	0.300
PbCO3-Buffer C-1	601	1.97E-04	1.34	10.07	0.800
PbCO3-Buffer C-2	601	1.96E-04	1.34	10.07	0.800
PbCO3-Buffer D-1	601	3.92E-04	2.07	10.30	1.200
PbCO3-Buffer D-2	601	3.84E-04	2.07	10.32	1.200
PbCO3-Buffer E-1	601	8.13E-04	3.2	10.66	1.800
PbCO3-Buffer E-2	601	7.86E-04	3.2	10.67	1.800
PbCO3-Buffer F-1	601	8.33E-04	3.58	10.79	2.000
PbCO3-Buffer F-2	601	8.90E-04	3.58	10.78	2.000

PbCO3-Buffer A-1	679	2.15E-05	0.154	9.81	0.100
PbCO3-Buffer A-2	679	2.05E-05	0.154	9.80	0.100
PbCO3-Buffer B-1	679	5.18E-05	0.49	9.88	0.300
PbCO3-Buffer B-2	679	5.06E-05	0.49	9.80	0.300
PbCO3-Buffer C-1	679	1.93E-04	1.34	10.04	0.800
PbCO3-Buffer C-2	679	1.90E-04	1.34	10.04	0.800
PbCO3-Buffer D-1	679	3.75E-04	2.07	10.27	1.200
PbCO3-Buffer D-2	679	3.99E-04	2.07	10.28	1.200
PbCO3-Buffer E-1	679	7.89E-04	3.2	10.62	1.800
PbCO3-Buffer E-2	679	7.95E-04	3.2	10.62	1.800
PbCO3-Buffer F-1	679	9.29E-04	3.58	10.73	2.000
PbCO3-Buffer F-2	679	9.35E-04	3.58	10.73	2.000
PbCO3-Buffer A-1	720	1.98E-05	0.154	9.81	0.100
PbCO3-Buffer A-2	720	1.96E-05	0.154	9.80	0.100
PbCO3-Buffer B-1	720	5.03E-05	0.49	9.80	0.300
PbCO3-Buffer B-2	720	5.01E-05	0.49	9.80	0.300
PbCO3-Buffer C-1	720	1.81E-04	1.34	10.04	0.800
PbCO3-Buffer C-2	720	1.89E-04	1.34	10.04	0.800
PbCO3-Buffer D-1	720	3.55E-04	2.07	10.26	1.200
PbCO3-Buffer D-2	720	3.66E-04	2.07	10.27	1.200
PbCO3-Buffer E-1	720	7.55E-04	3.2	10.62	1.800
PbCO3-Buffer E-2	720	7.64E-04	3.2	10.62	1.800

*Notice that the experimental data are not presented in the report, but the experimental data have been reviewed, and will be presented in the revised milestone report. For the data at 238 days, please see WIPP—Solubility—12 pages 10-11; for the data at 287 days, please see WIPP—Solubility—12 pages 65-66; for the data at 336 days, please see WIPP—Solubility—12 page 97; for the data at 385 days, please see WIPP—Solubility—21 page 31; for the data at 511 days, please see WIPP—Solubility—21 page 59; for the data at 601 days, please see WIPP—Solubility—21 page 96; for the data at 679 days, please see WIPP—Solubility—27 page 28; for the data at 720 days, please see WIPP—Solubility—27 page 54.

[A] pH readings obtained by using a pH electrode were first converted to hydrogen ion concentrations on molar scale (pcH) by applying correction factors (see SP 12-14, Roselle, 2012), 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_Tasks14-15_Modeling.xls.

Table 4. Equilibrium constants at infinite dilution at 25°C and 1 bar for the Na^+—Pb^{2+}—Cl^-—HCO_3^-—CO_3^{2-} system

Reactions	log K_s^o, log β_1^o, log β_2^o or log β_{11}^o	Reference and Remarks
$PbCO_3$(cerussite, cr) = Pb^{2+} + CO_3^{2-}	−13.65 ± 0.15 (2σ) [A]	This study, based on solubility of $PbCO_3$(cr) in the mixtures of $NaHCO_3$ and NaCl and in the mixtures of $NaHCO_3$ and Na_2CO_3
Pb^{2+} + CO_3^{2-} = $PbCO_3$(aq)	6.87 ± 0.09 (2σ)	Woosley and Millero (2013)
Pb^{2+} + $2CO_3^{2-}$ = $Pb(CO_3)_2^{2-}$	10.41 ± 0.18 (2σ)	Easley and Byrne (2011)
Pb^{2+} + CO_3^{2-} + Cl^- = $Pb(CO_3)Cl^-$	7.23 ± 0.74 (2σ)	Woosley and Millero (2013)

[A] In the modeling, the log K modeled is for the reaction $PbCO_3$(cr) + H^+ = Pb^{2+} + HCO_3^-, which can be converted to log K_s^o listed in Table 4 with the log K_2 in the database for the reaction HCO_3^- = H^+ + CO_3^{2-}, which is −10.3392.

Table 5. Pitzer interaction parameters at 25°C and 1 bar for the Na^+—Pb^{2+}—Cl^-—HCO_3^-—CO_3^{2-} system

Pitzer Binary Interaction Parameters					
Species *i*	Species *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	Reference
Na^+	$Pb(CO_3)_2^{2-}$	0.1975	1.74	−0.2105	This study
Na^+	$Pb(CO_3)Cl^-$	0.3799	0.29	0.1921	This study
Pitzer Mixing Interaction Parameters (theta parameter) and Interaction Parameters Involving Neutral Species (lambda and zeta parameters)					
Species *i*	Species *j*	Species *k*	λ_{ij} or θ_{ij}	ζ_{ijk}	Reference
HCO_3^-	$Pb(CO_3)_2^{2-}$		0.1476		This study
CO_3^{2-}	$Pb(CO_3)_2^{2-}$		0.2223		This study
Cl^-	$PbCO_3$(aq)		−0.02		Woosley and Millero (2013)
Na^+	$PbCO_3$(aq)	Cl^-	0	−0.145	Woosley and Millero (2013)

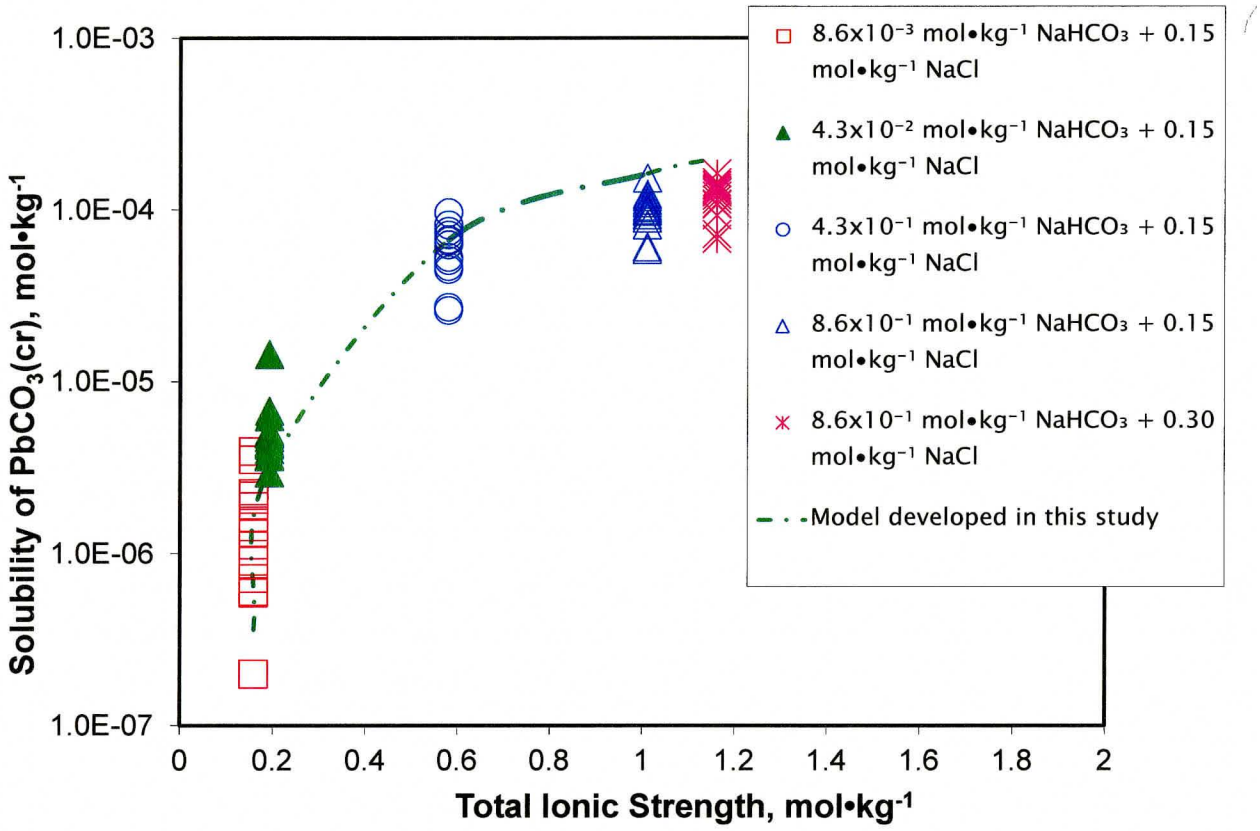

Figure 1. A plot showing solubilities of $PbCO_3$(cr) as a function of ionic strength on molal scale in $NaHCO_3$ solutions with 0.15–0.3 mol•kg^{-1} NaCl. The solubility curves are predicted using the model developed in this study.

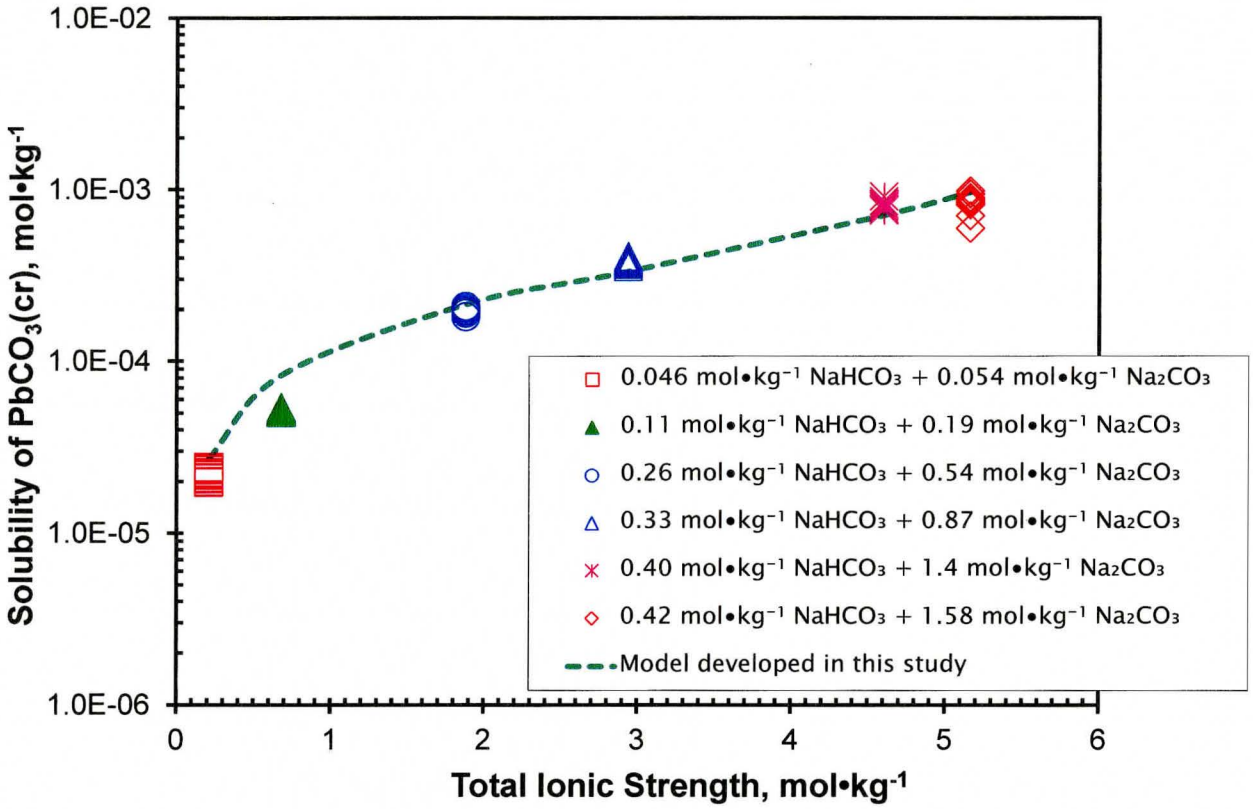

Figure 2. A plot showing solubilities of $PbCO_3$(cr) as a function of ionic strength on molal scale in the mixtures of $NaHCO_3$ + Na_2CO_3. The solubility curves are predicted using the model developed in this study.

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_Tasks14-15_Modeling.xls	In zip file AP154_Tasks14-15_DataPackage.zip, /nfs/data/CVSLIB/WIPP_EXTERNAL/ap154/Files
EQ3/6 DB DATA0.ox3	In zip file AP154_Tasks14-15_DataPackage.zip, /nfs/data/CVSLIB/WIPP_EXTERNAL/ap154/Files
EQ3/6 I/O files: pmH-1.3i through pmH-70.3i Buff-1.3i through Buff-80.3i VerE3-1.3i/o through VerE3-5.3i/o VCO3-1.3i/o through VCO3-6.3i/o	In zip file AP154_Tasks14-15_DataPackage.zip, /nfs/data/CVSLIB/WIPP_EXTERNAL/ap154/Files
Python input script for modeling: PbCO3_NaHCO3_NaHCO3-Na2CO3_logK_beta(1)set_PbCO3Cl_Pb(CO3)2.py	In zip file AP154_Tasks14-15_DataPackage.zip, /nfs/data/CVSLIB/WIPP_EXTERNAL/ap154/Files
Modeling Results: Results_AP154_Task14-15_rev1.xlsx	In zip file AP154_Tasks14-15_DataPackage.zip, /nfs/data/CVSLIB/WIPP_EXTERNAL/ap154/Files

3 RESULTS

Tables 4 and 5 provide the log K_s^o, and Pitzer parameter associated with log β_1^o, log β_2^o, log β_{11}^o in the Na^+—Pb^{2+}—Cl^-—$HCO3^-$—CO_3^{2-} system derived in this study. The parameters obtained in this work perform well in reproducing the experimental solubility data as demonstrated by Figure 1.

The log K_s^o (–13.65 ± 0.15 (2σ)) determined in this study is slightly lower than the value of –13.13 at infinite dilution determined by Nasanen et al. (1961), and the value of –13.15 ± 0.20 at infinite dilution, based on the value of –12.15 at 0.3 mol•dm^{-3} from Bilinski and Schindler (1982). In extrapolation of the value of Bilinski and Schindler (1982), the SIT coefficient from Powell et al. (2009) is used. The value provided by this study is considered more reliable than the previous values because the durations of the previous experiments lasted for only a few days, and the equilibrium may have not been attained. In contrast, the experimental data in this work are generated from the long-term experiments, up to 1,461 days. Therefore, in the light of those long-term experiments, experimental solubility data produced at Sandia National Laboratories Carlsbad Facility and the thermodynamic parameters obtained based on these data would provide an accurate descriptions about the interaction of lead with carbonate, and would have a direct impact on PA.

4 CONCLUSIONS

In this analysis report, the log K_s^o, and Pitzer parameter associated with log β_1^o, log β_2^o, log β_{11}^o in the Na^+—Pb^{2+}—Cl^-—$HCO3^-$—CO_3^{2-} system are obtained. With these parameters, the interactions of lead as radiation shielding material with carbonate in the brines can be accurately modeled.

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