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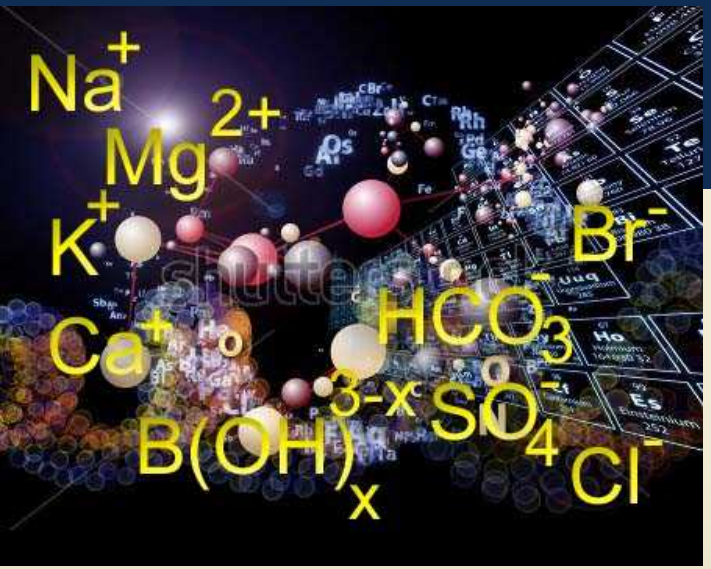

The Effect of Pb on Am(III) Solubility

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U.S. DEPARTMENT OF ENERGY
National Nuclear Security Administration

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OUTLINE OF PRESENTATION

- Literature Search for Lead Parameters
- Lead Sensitivity Analysis
- If Not Lead, Then What?

A LITERATURE SEARCH WAS PERFORMED

- DOE performed a systematic and thorough literature search regarding experimental solubility data on galena (PbS) to assess whether the existing literature experimental solubility data are suitable for development of a Pitzer model to describe the solubility behavior of galena under the conditions relevant to the WIPP.
- The literature search was initiated and performed well before the EPA comments communicated on December 12, 2015, via an e-mail (US EPA, 2015b).
- The literature search was performed by using WEB OF SCIENCE™ and Google Scholar®.
- The literature search covered original research studies published not only in English but also in foreign languages including Chinese, French, Japanese, and Russian.

A LITERATURE SEARCH WAS PERFORMED

- Based on this literature search, **DOE concluded that the existing experimental solubility data on galena are not suitable for development of a Pitzer model describing the solubility of galena under the conditions relevant to WIPP.**
- This can be attributed to any one or any combination of the following factors
  - (1) Experiments were performed at temperatures that are irrelevant to the WIPP.
  - (2) Experiments were performed at pH ranges that are not relevant to the WIPP.
  - (3) Experiments were performed at low ionic strengths that are not relevant to the WIPP, or at only one single ionic strength that prevent the evaluation of solubilities as a function of ionic strengths.
  - (4) Experimental conditions such as redox conditions were not well controlled.

EXAMPLE FROM THE LITERATURE SEARCH

Reference	Solutions Ionic Strengths and Temperatures	pcH, pmH or pH	Solid Phases	Evaluation and Disposition
Barrett and Anderson (1982)	(A) 1 m NaCl (I = 1 m) at 80°C (B) 2 m NaCl (I = 2 m) at 80°C (C) 3 m NaCl (I = 3 m) at 27°C, 60°C, and 95°C	(A) pH = 0.81-7.49 (B) Strongly acidic, pH < 2 (C) Strongly acidic, pH < 2.5	Galena and sphalerite	The experiments at 27°C could be relevant to the WIPP in terms of temperature. However, the experimental conditions are strongly acidic, which are not relevant to the WIPP. In addition, the measured pH readings were not corrected for the liquid junction potentials while the ionic strength (I ≥ 1.0 m) in the experiments was well above the dilute range valid for pH readings. Therefore, they cannot be used for the precise modeling.

Literature Search – 20 references reviewed

RESULTS OF THE LITERATURE SEARCH

Appendix B. Evaluations of Lab Studies for Solubility Data Concerning Galena (PbS)

Reference	Solution(s), Ionic Strength(s), and Temperature, °C	pH, pcH, or pmH	Solubility-Controlling Solid	Evaluation and Disposition
Anderson (1962)	(A) 0.11 M NaCl + 0.002 M NaOH (I = 0.112 M), saturated with H_2S(g) (B) 0.2 M NaCl + 1.0 M NaOH (I = 1.2 M), saturated with H_2S(g) T = 30°C to 90°C	(A) pH = 4.6 (B) pH = 7.9	Galena	The experiments at 30°C could be relevant to the WIPP in terms of temperature. Most of the experimental results were at acidic pH, which are not relevant to the WIPP conditions. The results at pH = 7.9 could be relevant. However, the measured pH readings were not corrected for the liquid junction potentials. As the ionic strength (I = 1.2 M) in the experiments was well above the dilute range valid for pH readings, corrections are required. Therefore, they cannot be used for the precise modeling.
Barrett and Anderson (1982)	(A) 1 m NaCl (I = 1 m) at 80°C (B) 2 m NaCl (I = 2 m) at 80°C (C) 3 m NaCl (I = 3 m) at 27°C, 60°C, and 95°C	(A) pH = 0.81-7.49 (B) Strongly acidic, pH < 2 (C) Strongly acidic, pH < 2.5	Galena and sphalerite	The experiments at 27°C could be relevant to the WIPP in terms of temperature. However, the experimental conditions are strongly acidic, which are not relevant to the WIPP. In addition, the measured pH readings were not corrected for the liquid junction potentials while the ionic strength (I ≥ 1.0 m) in the experiments was well above the dilute range valid for pH readings. Therefore, they cannot be used for the precise modeling.
Barrett and Anderson (1988)	3, 4, and 5 m NaCl (I = 3-5 m) from 25°C to 95°C	Strongly acidic, pH < 2	Galena and sphalerite	See remarks for Barrett and Anderson (1982).
Bondarenko (1968)	Fulvic acid solution at ambient temperature	pH = 1.90 to 10.06	Natural galena	The redox conditions of the experiments were not controlled. Therefore, they are not suitable for modeling.
Cama and Acero (2005)	DI water at 25°C	pH = 3	Galena, sludge galena	The redox conditions of the experiments were not controlled. Therefore, they are not suitable for modeling.

Appendix B continued on next page

Appendix B. Evaluations of Lab Studies for Solubility Data Concerning Galena (PbS) (Cont.).

Reference	Solution(s), Ionic Strength(s), and Temperature, °C	pH, pcH, or pmH	Solubility-Controlling Solid	Evaluation and Disposition
Comejo-Garrido et al. (2008)	(A) Water (B) 0.2 mM desferrioxamine-B ($C_{25}H_{48}N_6O_8$) Both at 25°C	pH = 5	Galena	The redox conditions of the experiments were not controlled. In addition, desferrioxamine-B is not relevant to the WIPP. Therefore, they are not suitable for modeling.
Giordano and Barnes (1979)	(A) 30°C, 0 and 1.0 m NaHS (B) 50°C, 0-2.85 m NaHS (C) 100°C, 0-2.85 m NaHS (D) 200°C, 0-2.85 m NaHS (E) 300°C, 0-2.85 m NaHS	pH were not measured	Galena	There is only one ionic strength (1.00 m NaHS) in addition to DI water, for the experiments around 30°C, which is of relevance to the WIPP in terms of temperature. However, the variation in ionic strength in the experiments is not sufficient for modeling with the Pitzer model.
Hamann and Anderson (1978)	(A) 0.0, and 3.0 m NaCl at 25°C (B) 0.0, 0.7, 0.9, 1.0, 2.7, 3.0 m NaCl at 90°C	(A) pH = 6.49-7.85 at 25°C (B) pH = 3.37-11.5 at 90°C	Galena	There is only one ionic strength (3.00 m NaCl) in addition to DI water, for the experiments at 25°C, which is of relevance to the WIPP. Hence, the variation in ionic strength in the experiments is not sufficient for modeling with the Pitzer model.

Appendix B continued on next page

Appendix B. Evaluations of Lab Studies for Solubility Data Concerning Galena (PbS) (Cont.).

Reference	Solution(s), Ionic Strength(s), and Temperature, °C	pH, pcH, or pmH	Solubility-Controlling Solid	Evaluation and Disposition
Hemley (1953)	(A) 0.10 M HCl (B) 0.097 M NaCl + 0.003M NaCl; 0.10 M NaCl + 0.001 M NaOH; 0.095 M NaCl + 0.007 M NaOH (C) 0.10 M, 1.00 M NaOH (D) 0.190 M Na_2S All at 25°C	(A) pH = 1.05 (B) pH = 2.5-5.5 (C) pH = 7.0, 7.9 (D) pH = 11.75	Galena	The experiments under the conditions (A), (B), and (D), are not relevant to the WIPP because of either acidic pH or extremely high pH (i.e., pH = 11.75). The experiments under the conditions (C) could be relevant to the WIPP in terms of pH, but the ionic strengths are not desirable because they are only up to 1 M, and there are only two data points, without a correction for the liquid junction potential for the experiment at I = 1 M . Therefore, they are not sufficient for parameterization for the WIPP thermodynamic model.
Malinin et al. (1989)	0.1-2 M NH_4Cl+NaCl from 350°C to 540°C	Not measured	Galena, pyrrhotite, and sphalerite	The experimental temperatures are irrelevant to the WIPP. Therefore, they are not suitable for modeling.
Nims and Bonner (1929)	Water at 25°C	Not mentioned	Galena	The redox conditions of the experiments were not controlled. Therefore, they are not suitable for modeling.
Nriagu (1971a)	1.0 m and 3.0 m NaCl at 90°C	pH = 2.00-6.74	Galena	The experimental temperature is irrelevant to the WIPP. Therefore, they are not suitable for modeling.
Nriagu (1971b)	3.0 m NaCl at (A) 28°C, (B) 60°C, (C) 90°C, (D) 120°C, and (E) 200°C	(A) pH = ~2 to ~4 (B) pH = ~2 to ~4 (C) pH = ~2.5 to ~4.5 (D) Not measured (E) Not measured	Galena	The experiments at 28°C could be relevant to the WIPP in terms of temperature. However, the experimental results were at acidic pH, and are not relevant to the WIPP conditions. In addition, pH readings were not corrected for liquid junction potentials, while the ionic strength was 3.0 m. Therefore, they are not suitable for modeling.

Appendix B continued on next page

Appendix B. Evaluations of Lab Studies for Solubility Data Concerning Galena (PbS) (Cont.).

Reference	Solution(s), Ionic Strength(s), and Temperature, °C	pH, pcH, or pmH	Solubility-Controlling Solid	Evaluation and Disposition
Pugh and Bergstrom (1986)	0.002 M $NaNO_3$ at 20-25°C	pH = 1-11	Galena	The redox conditions of the experiments were not controlled. In addition, there was only one single ionic strength and was low. Therefore, they are not suitable for modeling.
Uhler and Helz (1984)	0.10 M NaCl at 25°C, with the overall ionic strength of 0.16 M because of addition of EDTA	pH = 8.11-8.61	Galena	The experiments were conducted in a complex solution with one single, low ionic strength that is remote from those of the WIPP. Therefore, they are not suitable for the Pitzer model development. However, the solubility constant evaluated by the original authors is used for the sensitivity tests.
Villegas (2000)	(A) Na-NO_3-Cl-EDTA-TRIS (Tris-hydroxymethyl-aminomethane) (I = 0.017-0.170 M) (B) Na-Cl-EDTA (I = 0.106-0.160 M) (C) Na-NO_3-Acetate-TRIS (I = 0.010-0.282 M) All at 25°C	(A) pH = 7.40-11.38 (B) pH = 7.22-9.14 (C) pH = 4.37-8.49	Precipitated PbS; Galena	The experiments were conducted in complex solutions with low ionic strengths in a very narrow range that is remote from those of the WIPP. Therefore, they are not suitable for the Pitzer model development.

Appendix B continued on next page

Appendix B. Evaluations of Lab Studies for Solubility Data Concerning Galena (PbS) (Cont.).

Reference	Solution(s), Ionic Strength(s), and Temperature, °C	pH, pcH, or pmH	Solubility-Controlling Solid	Evaluation and Disposition
Wood et al. (1987)	0-5 m NaCl from 200°C to 350°C	pH not measured	Galena, pyrite, pyrrhotite, magnetite, sphalerite, gold, stibnite, bismuthinite, argentite, and molybdenite	The experimental temperatures are irrelevant to the WIPP. Therefore, they are not suitable for modeling.
Yao et al. (1992)	(A) 1.9 m NaCl only from 90°C to 210°C (B) 1.9 m NaCl + 0.2 m alkaline amino acid (lysine) from 90°C to 210°C	pH not measured	Galena	The experimental temperatures are irrelevant to the WIPP. Therefore, they are not suitable for modeling.
Yasui et al. (2011)	0.01, 0.1, 0.5, 1.0 m H_2SO_4 at T = 30°C to 170°C	pH = 0.04–1.83 at 30°C	Galena and anglesite ($PbSO_4$)	The experiments at 30°C could be relevant to the WIPP in terms of temperature. However, the experimental conditions are strongly acidic, which are not relevant to the WIPP. In addition, the measured pH readings for experiments at the ionic strength of 1.0 m were not corrected for the liquid junction potentials. Therefore, they are not suitable for the modeling.
Zhang et al. (2004)	1.0 M NaCl at (A) 25°C, (B) 50°C, (C) 75°C	(A) pH = 0.43-2.45 (B) pH = 0.43-2.03 (C) pH = 0.93-2.45	Galena	The experiments at 25°C could be relevant to the WIPP in terms of temperature. However, the experimental conditions are strongly acidic, which are not relevant to the WIPP. In addition, the measured pH readings for experiments at the ionic strength of 1.0 M were not corrected for the liquid junction potentials. Therefore, they are not suitable for the modeling.

LEAD SENSITIVITY ANALYSIS

In the sensitivity analysis, DOE created a provisional database called DATA0.FM3. The DATA0.FM3 was created by modifying DATA0.FM2 with addition of galena (PbS),

$$PbS(cr) + H^{+} = Pb^{2+} + HS^{-} \quad (1)$$

The equilibrium constant for the above reaction at 25°C and infinite dilution is taken from Uhler and Helz (1984). DOE is aware that Pb^{2+} could further form aqueous complexes with HS^{-},

$$Pb^{2+} + HS^{-} = PbHS^{+}, \quad (2)$$

$$Pb^{2+} + 2HS^{-} = Pb(HS)_2(aq) \quad (3)$$

$$Pb^{2+} + 3HS^{-} = Pb(HS)_3^{-} \quad (4)$$

LEAD SENSITIVITY ANALYSIS

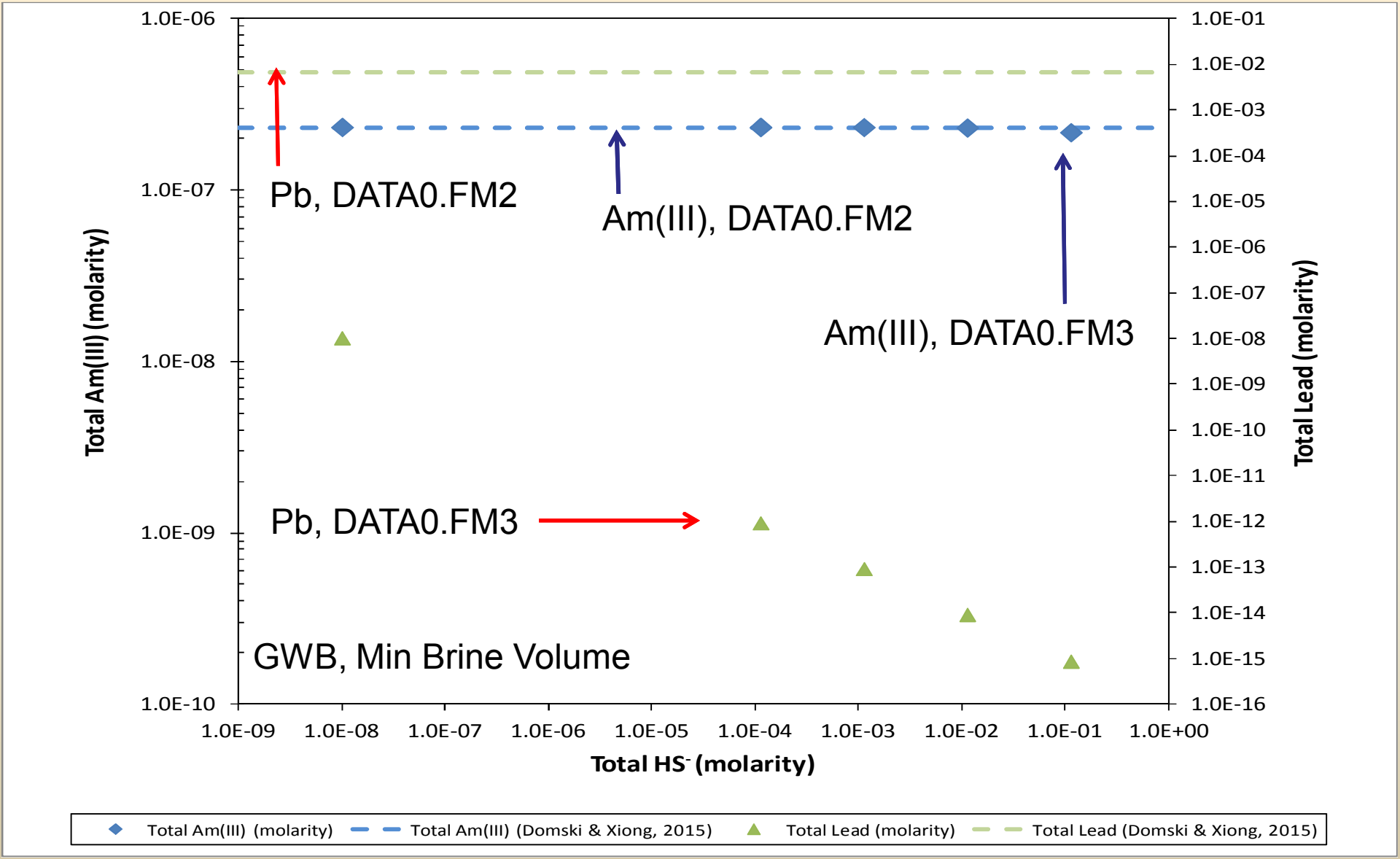
- DOE chose to include Reaction (1) only for the sensitivity analysis. There are two reasons behind this choice.
  - First, the sensitivity analysis using Reaction (1) only would tend to be conservative because the presence of Pb-bisulfide complexes would increase the solubility of PbS. In other words, solubilities of PbS tend to be under-predicted without Pb-bisulfide complexes.
  - Second, the values for Reactions (2) through (4) are not well defined currently.
- In the sensitivity analysis, DOE assumes that the total reduced sulfur (ΣHS^-) ranges from 10^{-4} M to 10^{-1} M.
  - This assumption is based on the observations that the concentrations of reduced sulfur in geological systems are in this range (Barnes, 1979).
  - In addition, DOE adds one more reduced sulfur concentration for testing, by assuming that the reduced sulfur concentrations are controlled by the stoichiometric dissolution of galena.

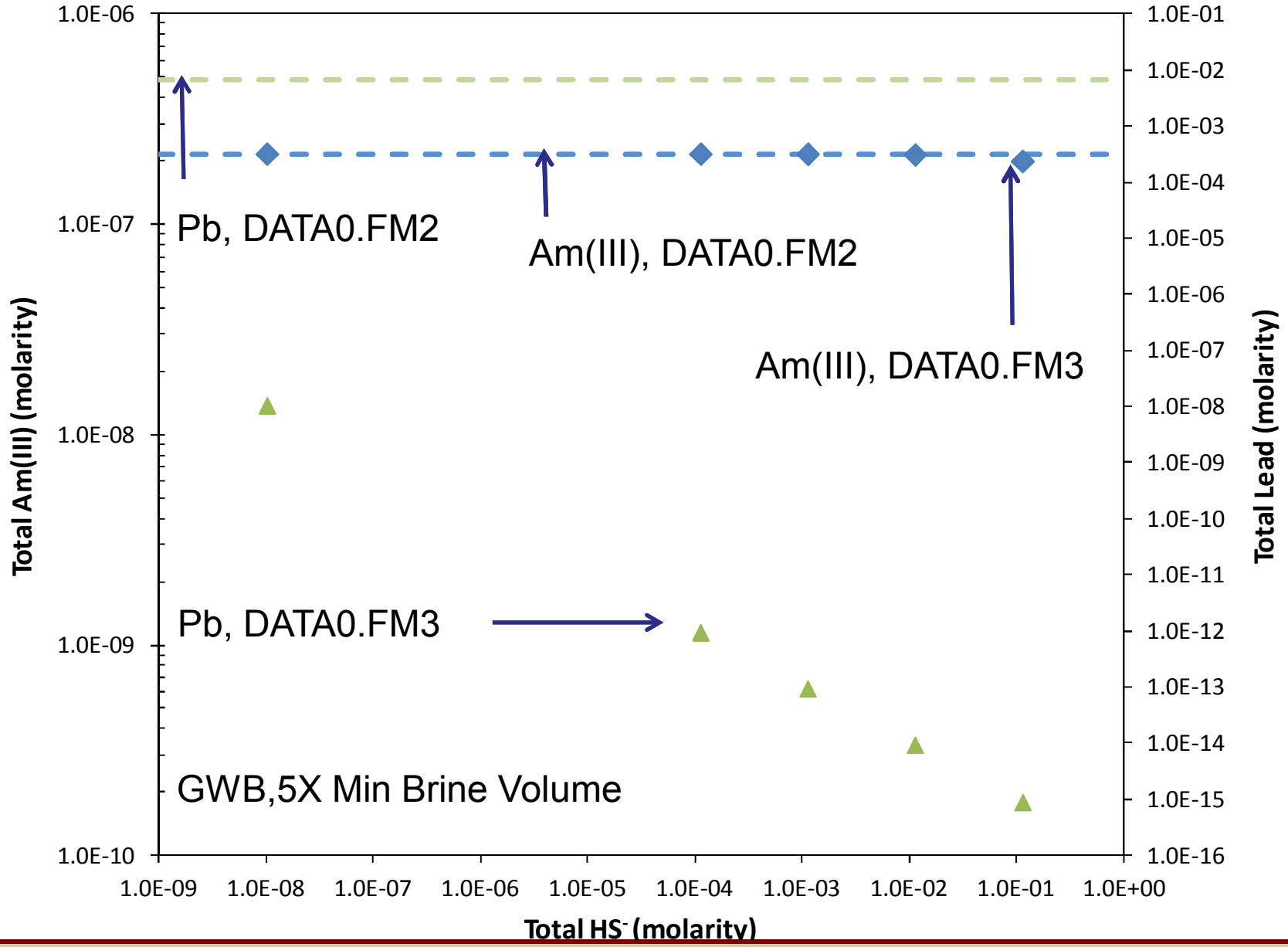
LEAD SENSITIVITY ANALYSIS

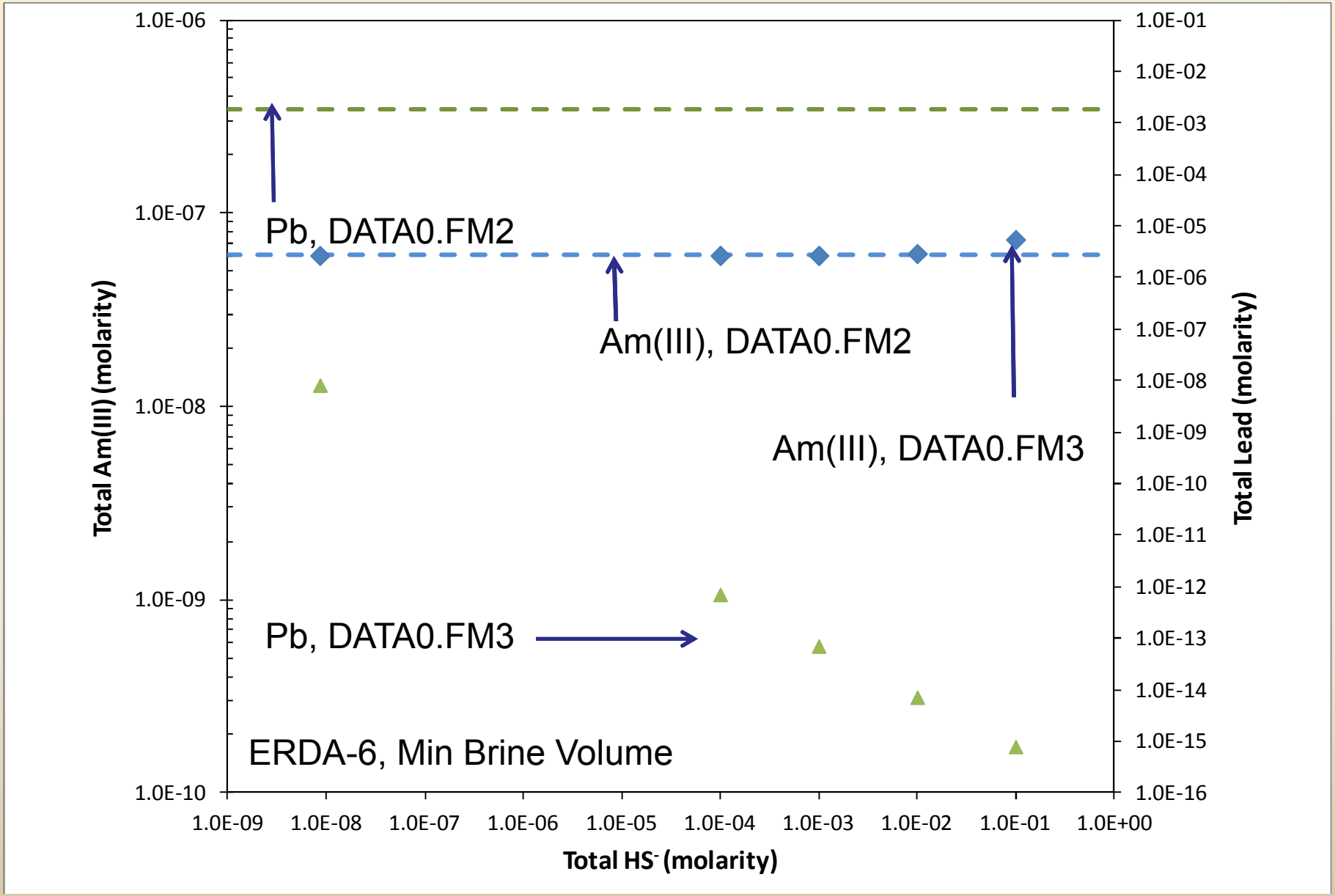
- In the sensitivity analysis, there are two dissolved concentrations of organic ligands in each brine (GWB and ERDA-6);
  - one in the minimum brine volume required for a DBR (direct brine release) and
  - one in the brine volume that is five times the minimum brine volume required for a DBR.
- The ΣHS^- concentrations are at 10^{-4} M, 10^{-3} M, 10^{-2} M, 10^{-1} M, and the one that is controlled by the stoichiometric dissolution of galena.
- Therefore, there are 20 computer simulations in total.

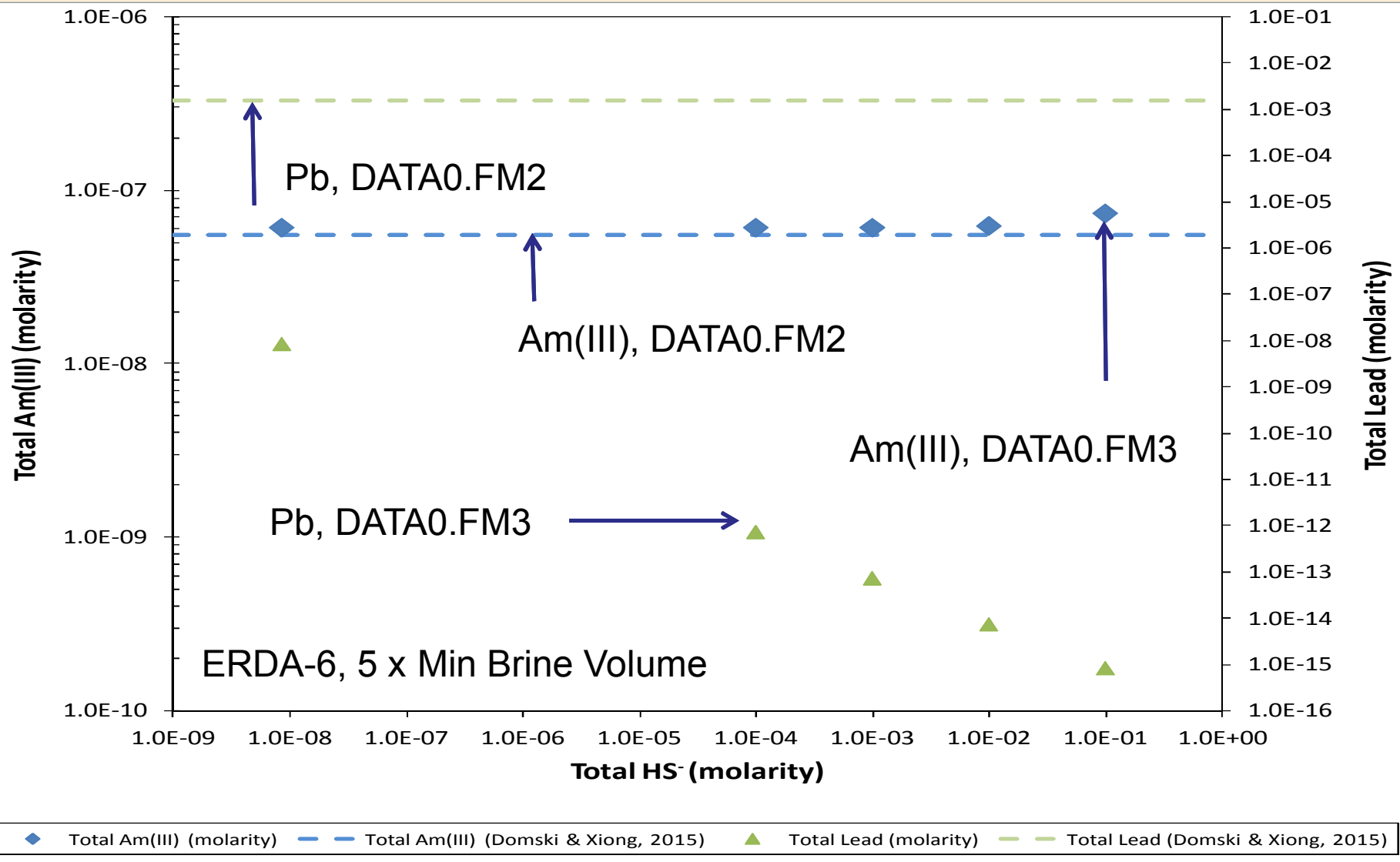
LEAD SENSITIVITY ANALYSIS

- In the next few slides the predicted Am(III) solubilities
  - as a function of ΣHS^- [and hence ΣPb(II)]
  - in equilibrium with galena
  - in GWB and ERDA-6
  - in the minimum brine volume required for a DBR (and 5 times the minimum)
- Also for comparison,
  - ΣAm(II) and ΣPb(II) from the baseline solubility calculations (Domski and Xiong, 2015) are also displayed using dashed lines.
- Of Note
  - The initial Pb-bearing phase is PbO (litharge) in Domski and Xiong (2015).


Pb, DATA0.FM2
Am(III), DATA0.FM2
Am(III), DATA0.FM3
Pb, DATA0.FM3
GWB, Min Brine Volume
Total Am(III) (molarity)
Total Lead (molarity)
Total HS- (molarity)
1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
1.0E-01
1.0E-02
1.0E-03
1.0E-04
1.0E-05
1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
1.0E-11
1.0E-12
1.0E-13
1.0E-14
1.0E-15
1.0E-16
1.0E-09
1.0E-08
1.0E-07
1.0E-06
1.0E-05
1.0E-04
1.0E-03
1.0E-02
1.0E-01
1.0E+00
Total Am(III) (molarity)
Total Am(III) (Domski & Xiong, 2015)
Total Lead (molarity)
Total Lead (Domski & Xiong, 2015)


1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
1.0E-01
1.0E-02
1.0E-03
1.0E-04
1.0E-05
1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
1.0E-11
1.0E-12
1.0E-13
1.0E-14
1.0E-15
1.0E-16
Total Am(III) (molarity)
Total Lead (molarity)
Pb, DATA0.FM2
Am(III), DATA0.FM2
Am(III), DATA0.FM3
Pb, DATA0.FM3
GWB,5X Min Brine Volume
1.0E-09
1.0E-08
1.0E-07
1.0E-06
1.0E-05
1.0E-04
1.0E-03
1.0E-02
1.0E-01
1.0E+00
Total HS⁻ (molarity)


1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
Total Am(III) (molarity)
1.0E-01
1.0E-02
1.0E-03
1.0E-04
1.0E-05
1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
1.0E-11
1.0E-12
1.0E-13
1.0E-14
1.0E-15
1.0E-16
Total Lead (molarity)
Pb, DATA0.FM2
Am(III), DATA0.FM2
Am(III), DATA0.FM3
Pb, DATA0.FM3
ERDA-6, Min Brine Volume
1.0E-09
1.0E-08
1.0E-07
1.0E-06
1.0E-05
1.0E-04
1.0E-03
1.0E-02
1.0E-01
1.0E+00
Total HS- (molarity)


Pb, DATA0.FM2
Am(III), DATA0.FM2
Am(III), DATA0.FM3
Pb, DATA0.FM3
ERDA-6, 5 x Min Brine Volume
Total Am(III) (molarity)
Total Lead (molarity)
Total HS- (molarity)
1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
1.0E-01
1.0E-02
1.0E-03
1.0E-04
1.0E-05
1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
1.0E-11
1.0E-12
1.0E-13
1.0E-14
1.0E-15
1.0E-16
1.0E-09
1.0E-08
1.0E-07
1.0E-06
1.0E-05
1.0E-04
1.0E-03
1.0E-02
1.0E-01
1.0E+00
Total Am(III) (molarity)
Total Am(III) (Domski & Xiong, 2015)
Total Lead (molarity)
Total Lead (Domski & Xiong, 2015)

LEAD SENSITIVITY ANALYSIS

- Based on this sensitivity analysis, **DOE concludes that Am(III) solubilities are NOT sensitive to the concentration of Pb and are NOT under-predicted in Domski and Xiong (2015) owing to the presence of Pb species.**

IF NOT LEAD, THEN WHAT?

- The Am(III) solubilities predicted by Domski and Xiong (2015) using DATA0.FM2 are indeed lower than those predicted by Brush and Domski (2014) using DATA0.FM1, as correctly noted by EPA (U.S. EPA, 2015b).
- The decrease in Am(III) solubilities is actually attributed to an improvement and refinement of the stability constant for $CaEDTA^{2-}$ and its associated Pitzer interaction parameters,

$$Ca^{2+} + EDTA^{4-} = CaEDTA^{2-} \qquad \text{(III-15)}$$

IF NOT LEAD, THEN WHAT?

- In DATA0.FM1, the log β^o_1 value of 10.1260 for Reaction (III-15) was based on the value for $MgEDTA^{2-}$, using $MgEDTA^{2-}$ as an analog to $CaEDTA^{2-}$

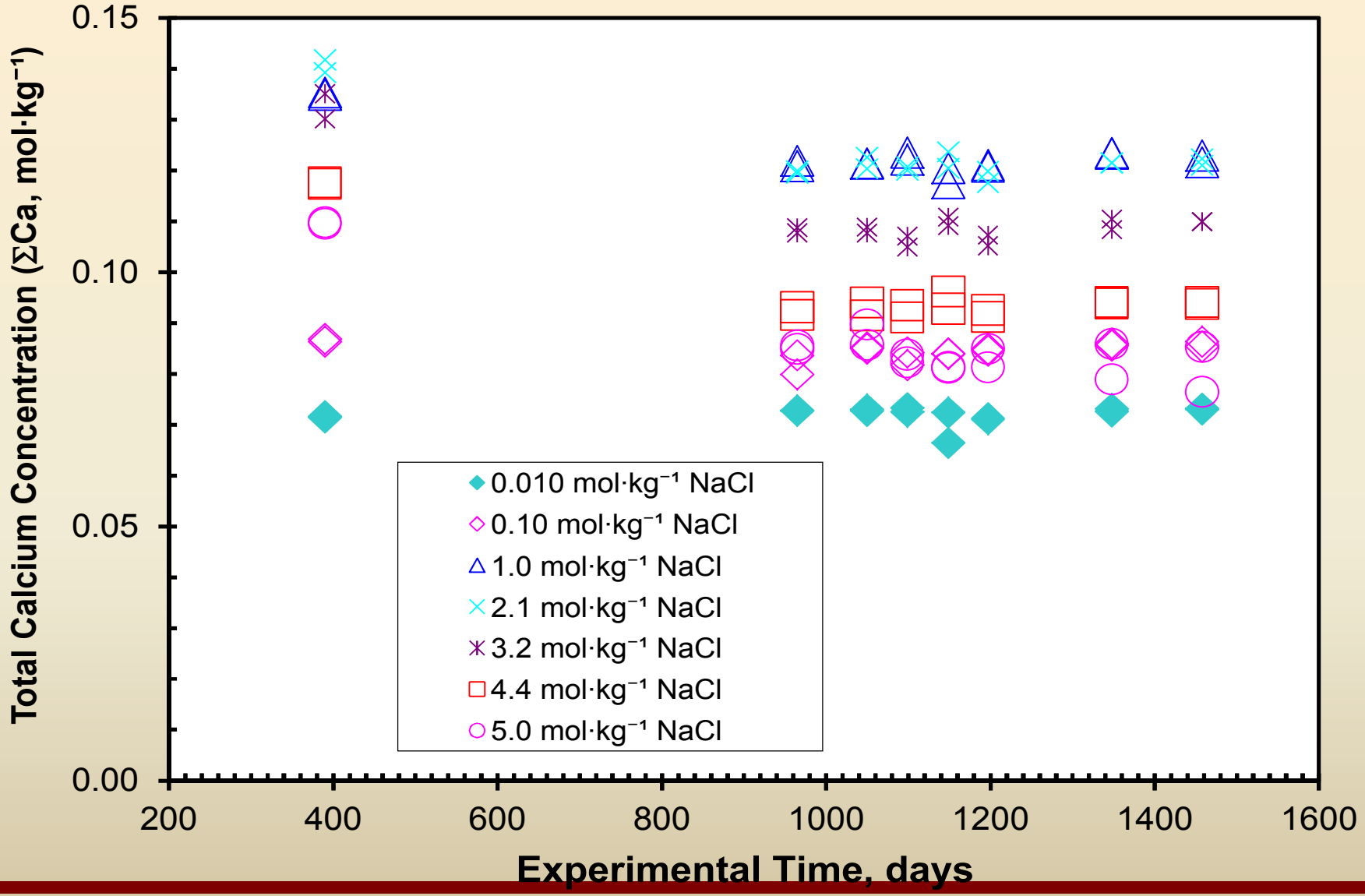
$$Mg^{2+} + EDTA^{4-} = MgEDTA^{2-} \qquad \text{(III-13)}$$

- In DATA0.FM2, the log β^o_1 value of 11.1562 for Reaction (III-15) was based on solubility data for $Ca_2EDTA(s)$ in NaCl and $MgCl_2$ solutions recently produced at Sandia National Laboratories (Xiong 2015a, 2015b, 2015c).
- The log β^o_1 value of 11.1562 for Reaction (III-15) is in excellent agreement the value experimentally determined by Carini and Martell (1954) of 10.98.

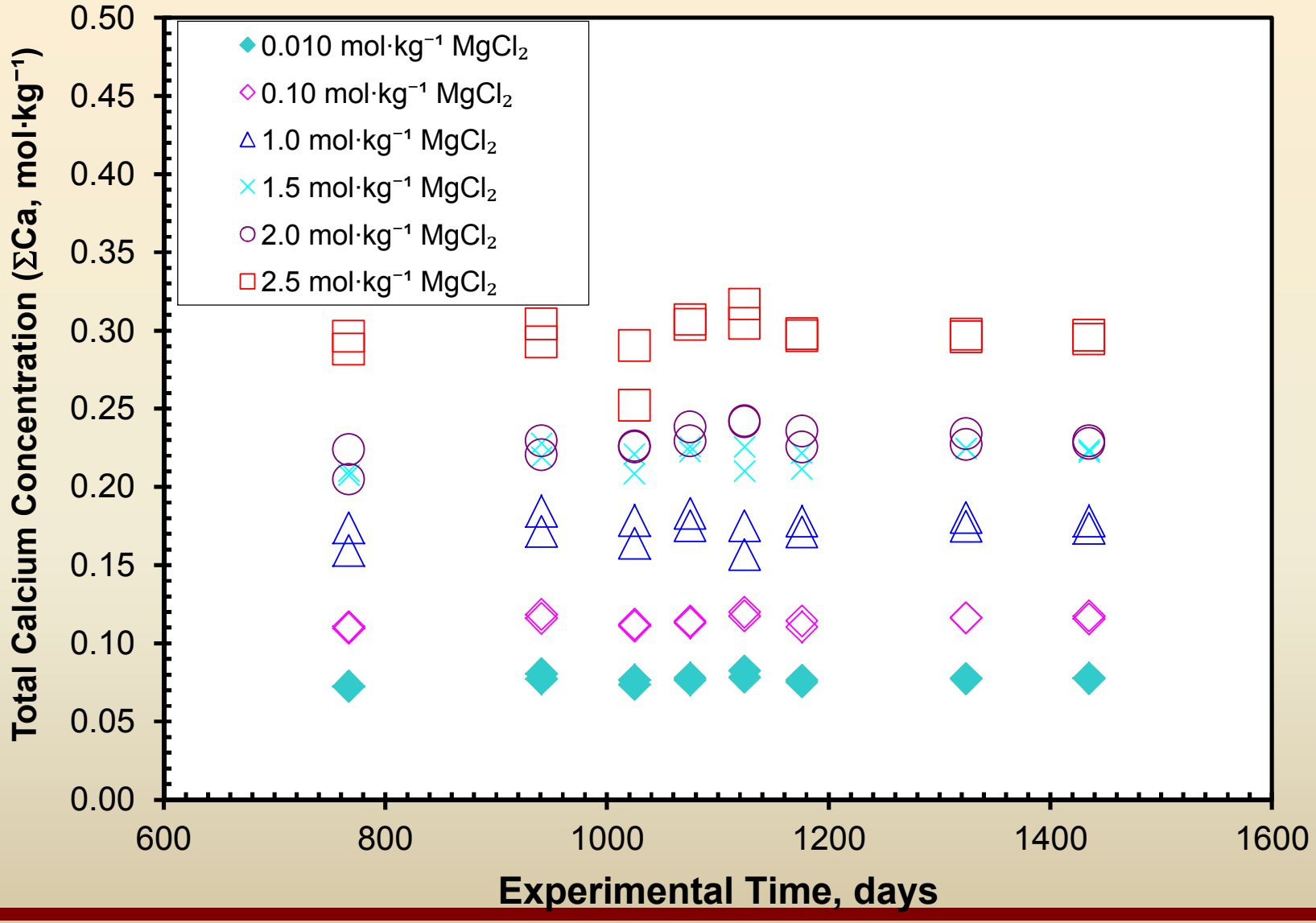
IF NOT LEAD, THEN WHAT?

- In DATA0.FM1, the Pitzer interaction parameters for Na^+–$CaEDTA^{2-}$ were assumed to be the same as those for Na^+–$MgEDTA^{2-}$, again using the interactions of Na^+–$MgEDTA^{2-}$ as analogs for Na^+–$CaEDTA^{2-}$.
- In the DATA0.FM2, DOE evaluated the Pitzer parameters for Na^+–$CaEDTA^{2-}$ based on solubility data for $Ca_2EDTA(s)$ in NaCl and MgCl2 solutions recently produced at Sandia National Laboratories (Xiong 2015a, 2015b, 2015c).
- In the DATA0.FM1, there were no Pitzer interaction parameters for Mg^{2+}–$CaEDTA^{2-}$.
- In the DATA0.FM2, DOE evaluated the Pitzer interaction parameters for Mg^{2+}–$CaEDTA^{2-}$ based on solubility data for $Ca_2EDTA(s)$ in NaCl and $MgCl_2$ solutions recently produced at Sandia National Laboratories (Xiong 2015a, 2015b, 2015c).

IF NOT LEAD, THEN WHAT?



IF NOT LEAD, THEN WHAT?

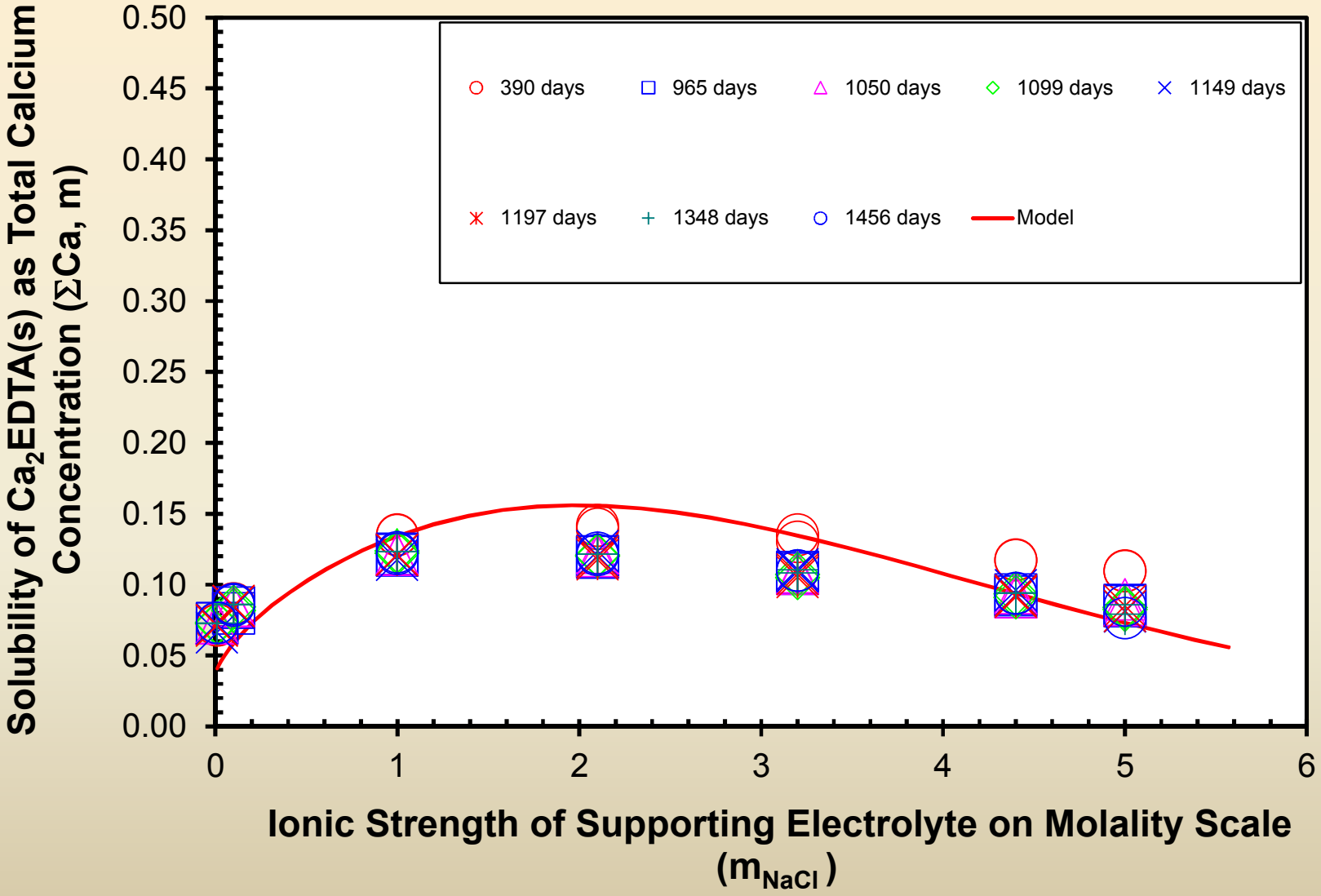


IF NOT LEAD, THEN WHAT?

Table 1. 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	1.74	0.0131	This work
Mg^{2+}	$CaEDTA^{2-}$	0.525	3.27	0	This work
Ca^{2+}	$MgEDTA^{2-}$	0.08436	3.27	0	This work
Mg^{2+}	$EDTA^{4-}$	–0.01	11.6	0.3	This work
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

IF NOT LEAD, THEN WHAT?



IF NOT LEAD, THEN WHAT?

- With the addition of a refined log β^{o}_{1} for $CaEDTA^{2-}$ and its associated Pitzer parameters to the database,
  - $CaEDTA^{2-}$ becomes the dominant species interacting with EDTA.
  - This in turn significantly reduces the contribution of $AmEDTA^{-}$ to the total Am(III) solubilities.
  - Therefore, the decrease in Am(III) solubilities is caused by the reduced contributions of $AmEDTA^{-}$.

CONCLUSIONS

- DOE concludes that:
  - The WIPP thermodynamic database has been updated to reflect the advances in chemistry/geochemistry relevant to WIPP conditions since CRA-2009.
  - The decrease in Am(III) solubilities predicted using DATA0.FM2 is attributed to the improved and refined parameterization for $CaEDTA^{2-}$