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to: The WIPP Record Center

from: Yongliang Xiong and Paul Domski
Repository Performance Department 6932
Yongliang Xiong and Holly P. Nelson for

subject: A Sensitivity Analysis of Am(III) Solubilities as a Function of Concentration of Total Reduced Sulfur (ΣHS^-) (and hence $\Sigma Pb(II)$) in the Presence of Galena (PbS)

In the e-mail sent by EPA on December 15, 2015 (U.S. EPA, 2015), EPA hypothesizes that the omission of galena (PbS) from DATA0.FM2 is the cause of lower Am(III) baseline solubility. In the e-mail, U.S. EPA stated (U.S. EPA, 2015),

> *...did not include lead sulfide solids or aqueous lead-sulfide speciation. Because abundant H2S will be present in the repository, omitting lead-sulfide solids and aqueous species is not representative of expected repository conditions. Omitting lead sulfides is likely to cause underestimations of the americium(III) solubilities...*

To investigate this hypothesis, we performed a sensitivity analysis as follows.

In the sensitivity analysis, we 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 infinite dilution is taken from Uhler and Helz (1984). We are aware that Pb^{2+} could further form aqueous complexes with HS^-,

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

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

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

We 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. Second, the values for Reactions (2) through (4) are not well defined currently.

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In the sensitivity analysis, we assume 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, we add one more reduced sulfur concentration for testing, by assuming that the reduced sulfur concentrations are controlled by the stoichiometric dissolution of galena.

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. Those concentrations are identical to those used for the baseline solubility calculations (Domski and Xiong, 2015). The ΣHS^- concentrations used 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. In Figure 1, the predicted Am(III) solubilities as a function of ΣHS^- [and hence ΣPb(II)] in equilibrium with galena in GWB in the minimum brine volume required for a DBR are displayed. For comparison, ΣAm(II) and ΣPb(II) from the baseline solubility calculations (Domski and Xiong, 2015) are also displayed in Figure 1, and they are represented by the dashed lines. Notice that the initial Pb-bearing phase in the baseline solubility calculations is PbO (litharge). Figure 1 demonstrates that Am(III) solubilities are insensitive to both of ΣPb(II) and ΣHS^-. This is also true with all of the other test cases (see Figure 2, Figure 3, Figure 4).

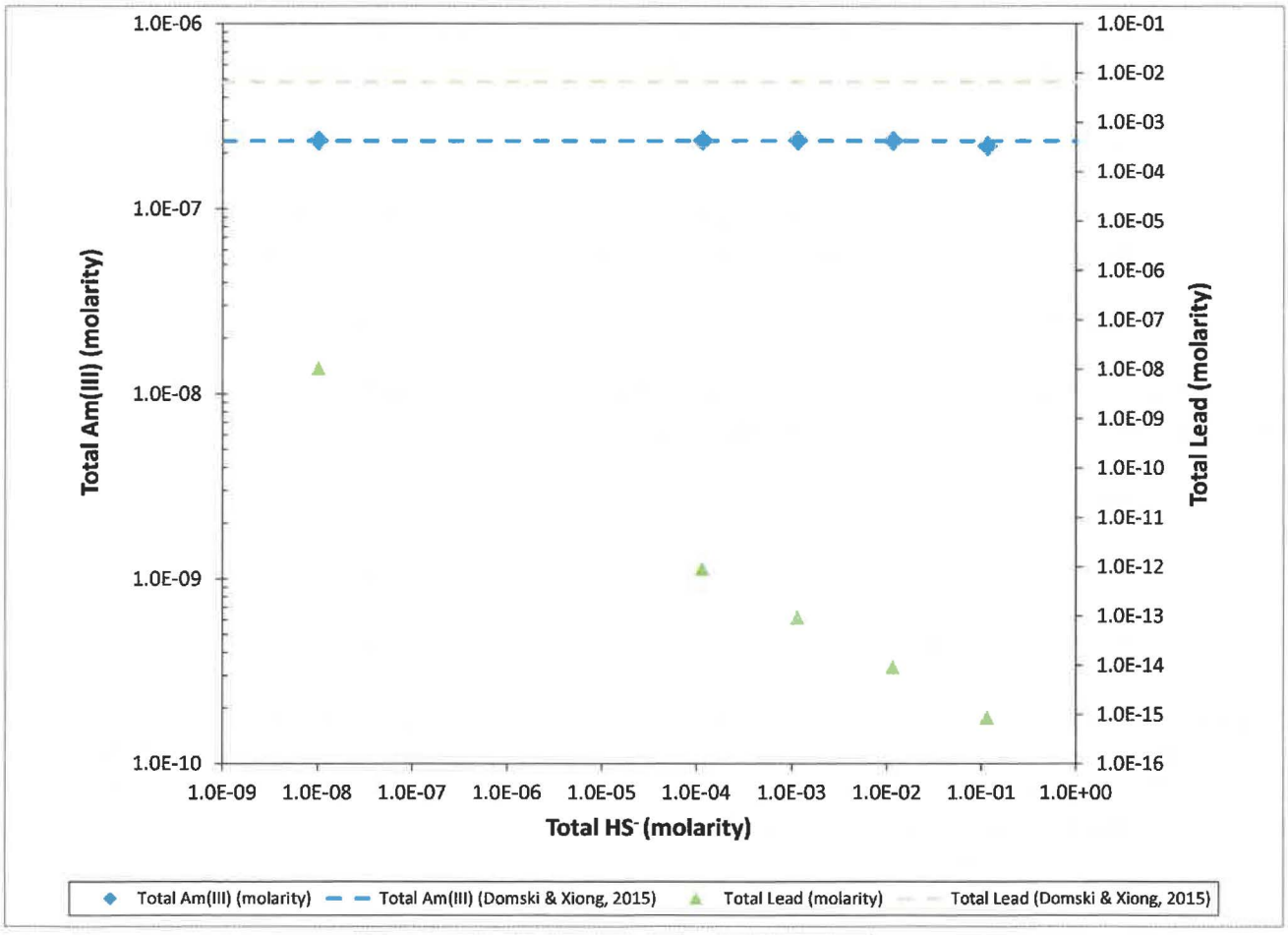

Figure 1. A plot showing solubilities of Am(III) as a function of concentrations of total reduced sulfur (ΣHS^-) and lead ($\Sigma Pb(II)$), for GWB with dissolved concentrations of organic ligands in the minimum brine volume required for a DBR (direct brine release).

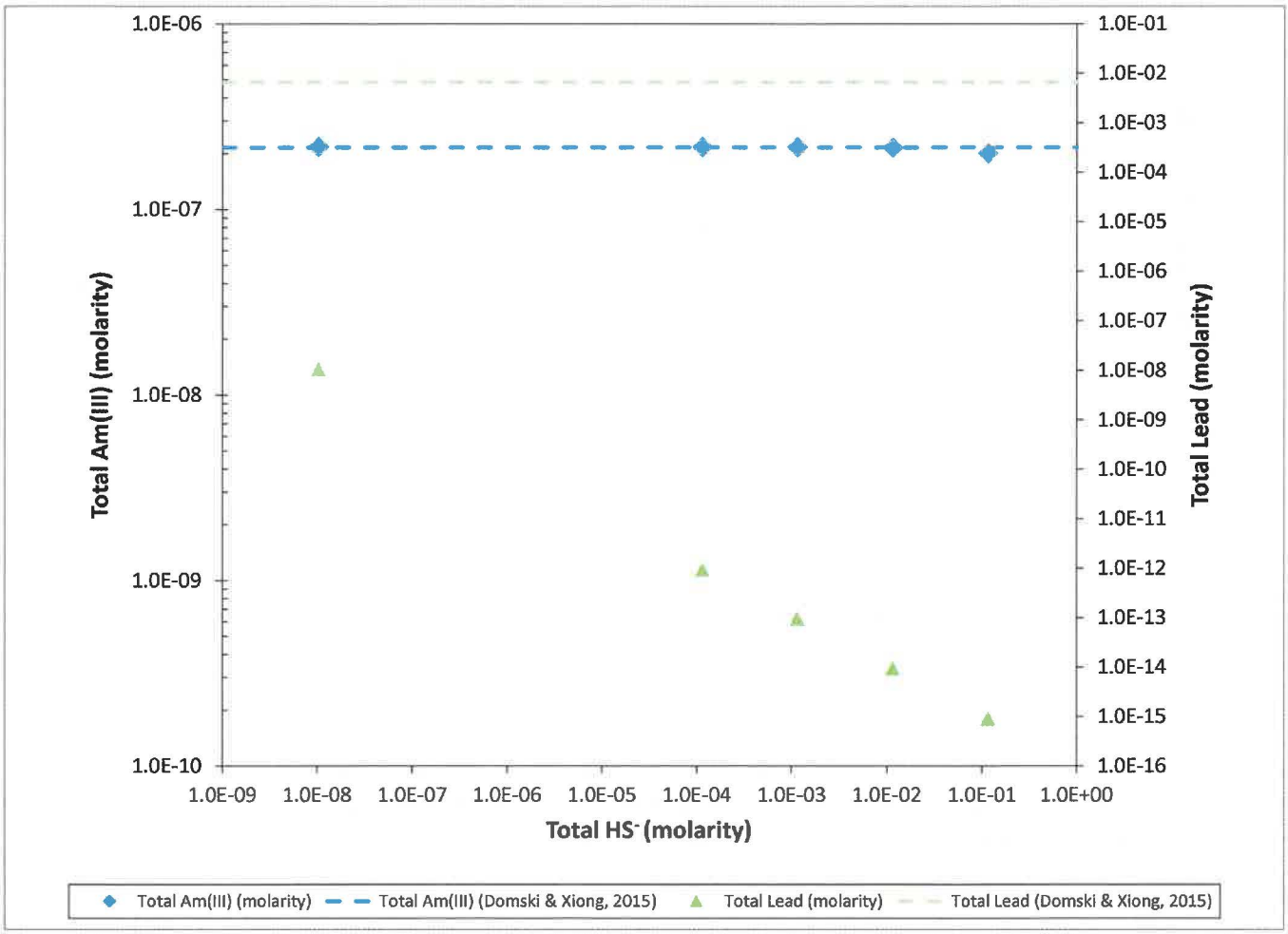

Figure 2. A plot showing solubilities of Am(III) as a function of concentrations of total reduced sulfur (ΣHS^-) and lead ($\Sigma Pb(II)$), for GWB with dissolved concentrations of organic ligands in the brine volume that is five times of the minimum brine volume required for a DBR (direct brine release).

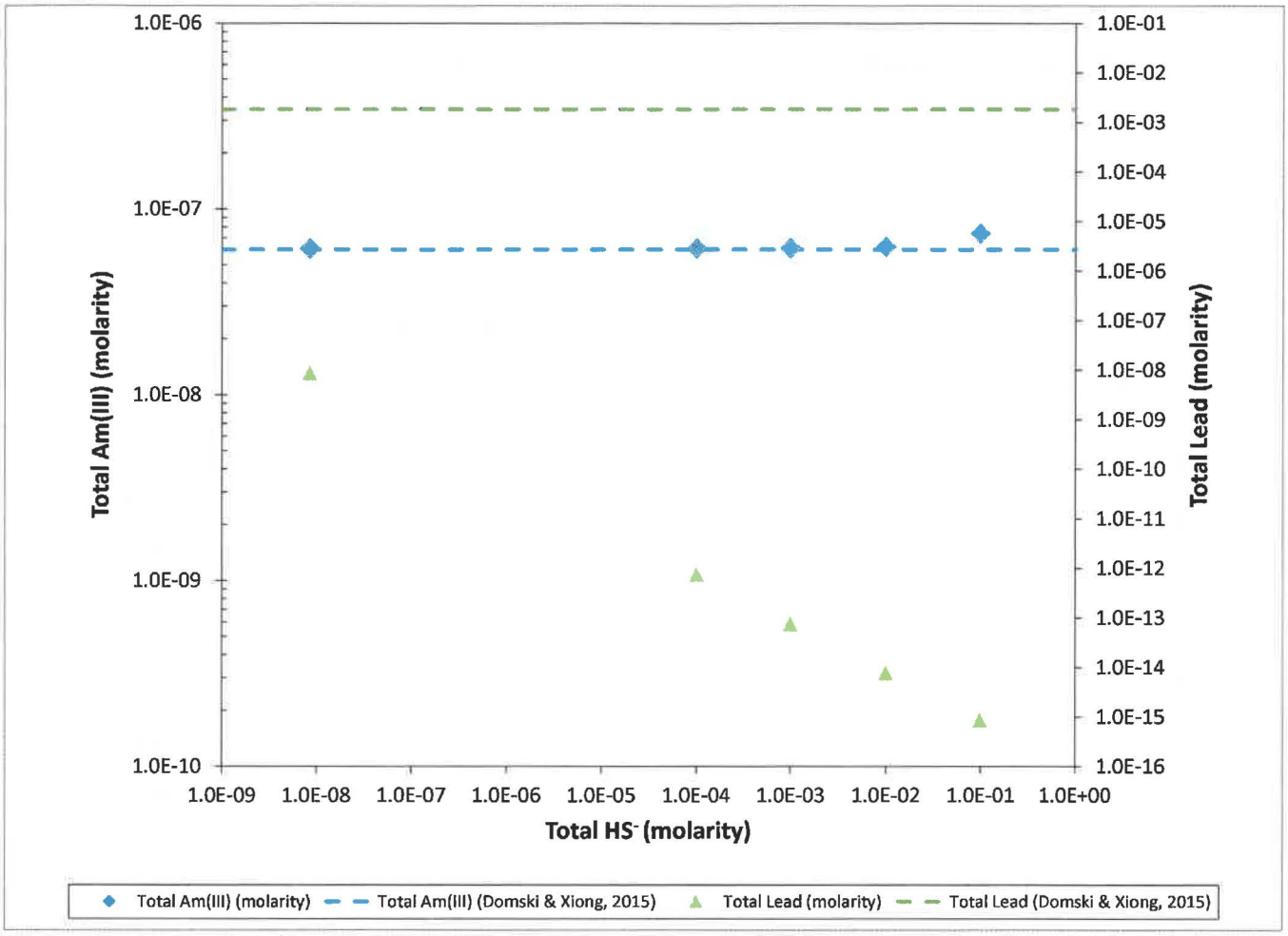

Figure 3. A plot showing solubilities of Am(III) as a function of concentrations of total reduced sulfur (ΣHS^-) and lead ($\Sigma Pb(II)$), for ERDA-6 with dissolved concentrations of organic ligands in the minimum brine volume required for a DBR (direct brine release).

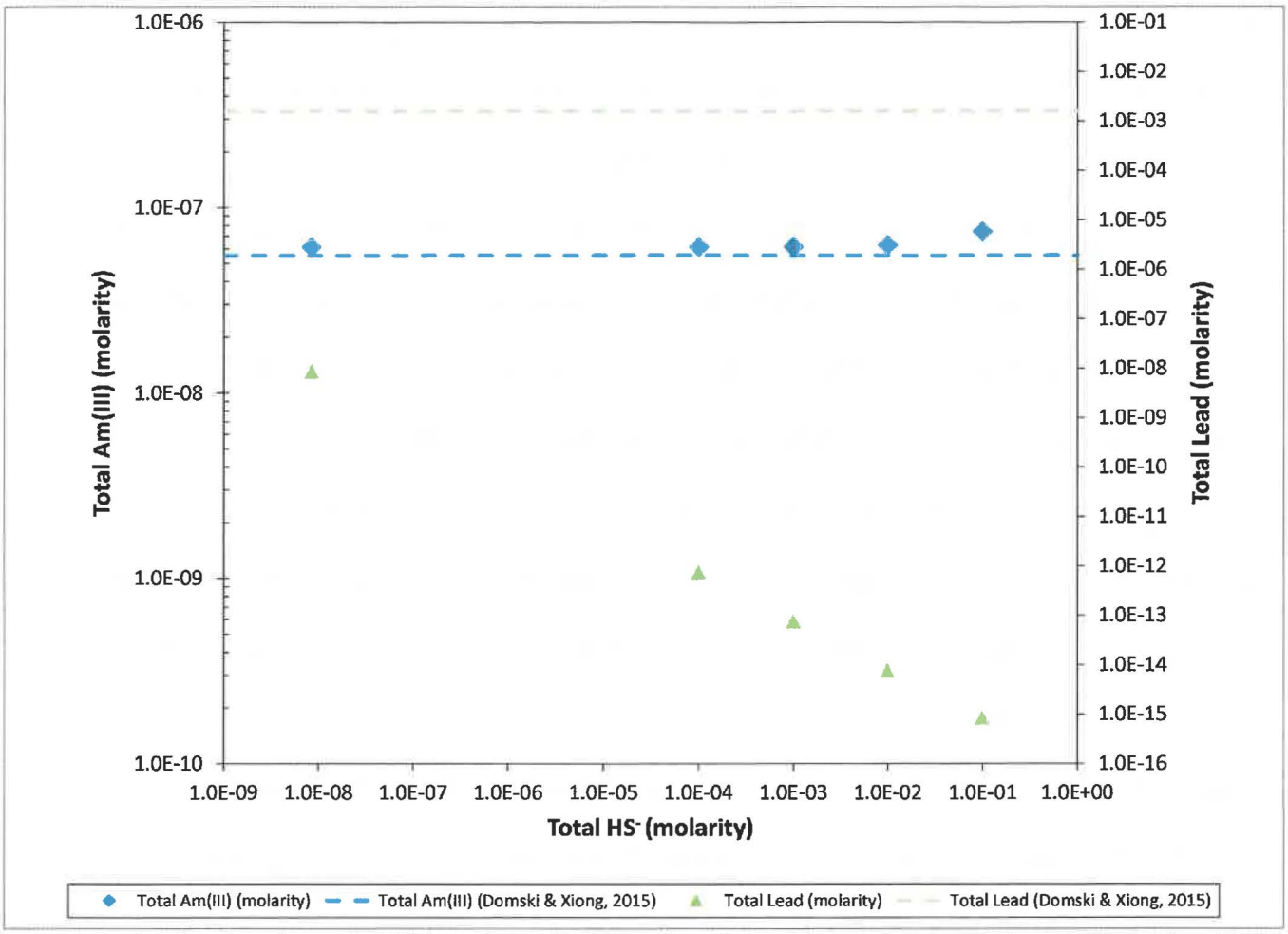

Figure 4. A plot showing solubilities of Am(III) as a function of concentrations of total reduced sulfur (ΣHS^-) and lead ($\Sigma Pb(II)$), for ERDA-6 with dissolved concentrations of organic ligands in the brine volume that is five times of the minimum brine volume required for a DBR (direct brine release).

Based on the sensitivity analysis, we concluded that Am(III) solubilities were not under-predicted in Domski and Xiong (2015) owing to the presence of Pb species.

The EQ3/6 computer simulations for this sensitivity analysis were performed by using EQ3/6 Version 8.0a (Wolery et al., 2010; Xiong, 2011). All files are located at /nfs/data/CVSLIB/WIPP_SPECIAL_ANALYSES/PbSsensitivity.

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