

RAI: Volume 3, Chapter 2.2.1.3.4, First Set, Number 9, Supplemental:

Justify the use of high-temperature Pu solubility experimental data in fitting the adjusted-Eh Pu solubility abstraction as it applies to all repository thermal conditions.

Basis: The Eh-pH equation used in the adjusted-Eh abstraction for the Pu concentration limit was selected so that the resulting curve of Pu concentration versus pH passes through a set of published Pu solubility experimental results (SAR Figure 2.3.7-37). Some of the data used in SAR Figure 2.3.7-37, however, were obtained at temperatures of 60° and 90° C (Nitsche, et al., 1993, 1994; Efurud, et al. 1998), which are higher than long-term conditions in the waste package. For Pu, higher temperatures result in lower solubility limits (SNL, 2007a, Section 6.3.3.3) and therefore lower release rates. The high-temperature data, therefore, may inappropriately skew the range of experimental data to lower values. Without the 60° and 90° C results, nearly every data point in SAR Figure 2.3.7-37 falls above the mean curve that was apparently fit through the data. The requested information is needed to verify compliance with 10 CFR 63.21(c)(11)-(15) and 63.114(a) and (b).

1. RESPONSE

The high-temperature plutonium solubility experimental data were not used to fit the adjusted-Eh plutonium solubility abstraction. The experimental data that were used to fit the adjusted-Eh plutonium solubility model were taken at 22°C by Rai (1984). The 60°C and 90°C temperature data points from work by Nitsche et al. (1993 and 1994) and Efurud et al. (1998) were not used to create the adjusted-Eh solubility model, because they are not relevant to long-term conditions in the waste package and they represent lower solubilities than data at ambient temperature. As discussed in SAR Section 2.3.7.13.3, the solubility modeling of actinides was at 25°C. Therefore, the results modeled with the adjusted-Eh plutonium solubility model predict release rates relevant to long-term conditions in the waste package.

As requested by the NRC staff at the clarification meeting on April 1, 2009, additional information regarding the establishment of the Eh-pH relation for the adjusted-Eh solubility model is provided. The adjusted-Eh solubility model was developed based on examination of experimental data and repository-relevant conditions. As discussed in SAR Section 2.3.7.10.3.1, plutonium solubility calculated at an atmospheric fO_2 of 0.2 bar is significantly above the measured solubility from experiments (Efurud et al. 1998; Nitsche et al. 1993 and 1994; Rai 1984; Rai et al. 2001). Furthermore, the predicted plutonium species using atmospheric fO_2 of 0.2 to calculate Eh were not consistent with these experimental data. For example, the dominant plutonium species is Pu(V) in experiments conducted by others for pH from 3.5 to 5 (Rai 1984) and for pH from 6 to 8.5 (Nitsche et al. 1993 and 1994). In natural waters, plutonium(V) is observed to be the dominant dissolved species (Choppin et al. 1986). However, as shown in *Dissolved Concentration Limits of Elements with Radioactive Isotopes* (SNL 2007, Figure V-5), the oxidation state distribution in the solubility modeling results using $fO_2 = 0.2$ bars, shows that Pu(VI) is the dominant species over the entire pH range modeled. Therefore, the plutonium

solubility model using atmospheric fO_2 of 0.2 bars does not adequately represent plutonium behavior in aqueous systems because the solubility model (due to differing oxidation states of plutonium) is sensitive to redox potential. The discrepancy between the plutonium solubility model prediction results using atmospheric fO_2 and solubility experiments, as well as plutonium species observed in natural waters, led to the development of the adjusted-Eh solubility model.

As discussed in *Dissolved Concentration Limits of Elements with Radioactive Isotopes* (SNL 2007), further refinement of the solubility model was obtained by incorporating experimental data results from natural waters. Baas Becking et al. (1960) analyzed 6,200 Eh and pH measurements in natural waters and found that for pH between 3.2 and 12.6 there is an upper boundary for Eh-pH conditions that is shown in equation 1 (Baas Becking et al. 1960). Equation 1 is a more realistic boundary of redox conditions in natural waters that are in contact with the atmosphere than using atmospheric oxygen fugacity alone (Krauskopf and Bird 1995).

$$Eh = 1.04 - 0.0592 \text{ pH} \quad (\text{Eq. 1})$$

Comparison of predicted plutonium solubility, using Eh calculated from Equation 1, and experimental data on plutonium solubility is shown in Figure 1. While most of the measured plutonium solubility data fall within the uncertainty range of the model, the mean modeled plutonium concentration is below most of the experimental results taken at ambient temperature. Furthermore, some of the experimental data fall above the upper bound set by the Eh solubility model when Equation 1 is used. Therefore, the adjusted-Eh solubility model was developed because the modeled plutonium solubility results using Eh calculated from Equation 1 are lower than the experimental solubility results.

As discussed in SAR Section 2.3.7.10.3.1, the adjusted-Eh solubility model uses Eh calculated as shown in Equation 2. This adjusted-Eh equation was derived by adding 0.06 volts to the calculated Eh value given in Equation 1 for pH values between 3.2 and 12. The rationale for adding 0.06 volts is that measured Eh data from Rai (1984) are about 0.06 volts higher than values obtained from Equation 1. Thus, the Rai (1984) data that are measured at 22°C were used to fit the adjusted-Eh plutonium solubility model.

$$Eh = 1.10 - 0.0592 \text{ pH} \quad (\text{Eq. 2})$$

Using the adjusted-Eh solubility model, most of the data points from the solubility experiments fall within the uncertainty range of the adjusted-Eh solubility model, as shown in Figure 2. As requested by the NRC, Figure 2 (from SAR Figure 2.3.7-37) has been created without the high-temperature data. Note, there is no change to the modeled plutonium solubility results due to the fact that the high-temperature data were not used in the development of the adjusted-Eh solubility model.

Plausible explanations for the higher apparent plutonium solubility in experimental data include colloid formation and high ionic strengths. For example, measured aqueous plutonium concentrations are not only true dissolved plutonium, but contain plutonium colloids or polymers that are not excluded by the filter size. Kim and Kanellakopoulos (1989) reported that a large percent of plutonium was in plutonium(IV) colloid form even though the filter size was as small

as 1 nm. Experimental solutions used by Rai et al. (2001) had higher ionic strengths than that modeled, which also yields a higher solubility.

In summary, the development of the adjusted-Eh solubility model is based upon experimental Eh data on natural waters, plutonium solubility, and speciation. The high-temperature plutonium solubility experimental data presented in SAR Figure 2.3.7-37 were not used for model development. Only data at 22°C reported by Rai (1984) were used to fit the adjusted-Eh solubility model. Thus, the adjusted-Eh solubility model appropriately represents the range of experimental data consistent with the long-term conditions in the waste package.

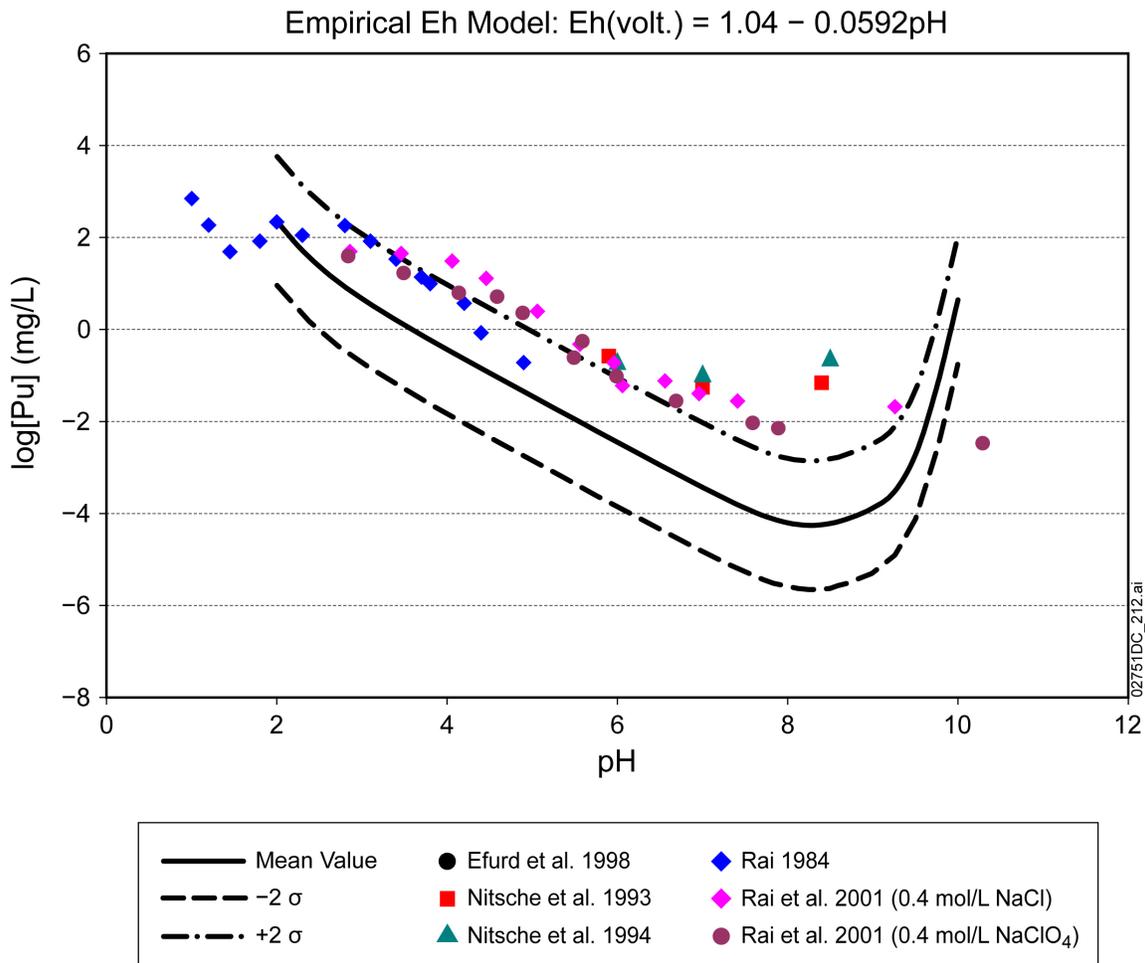
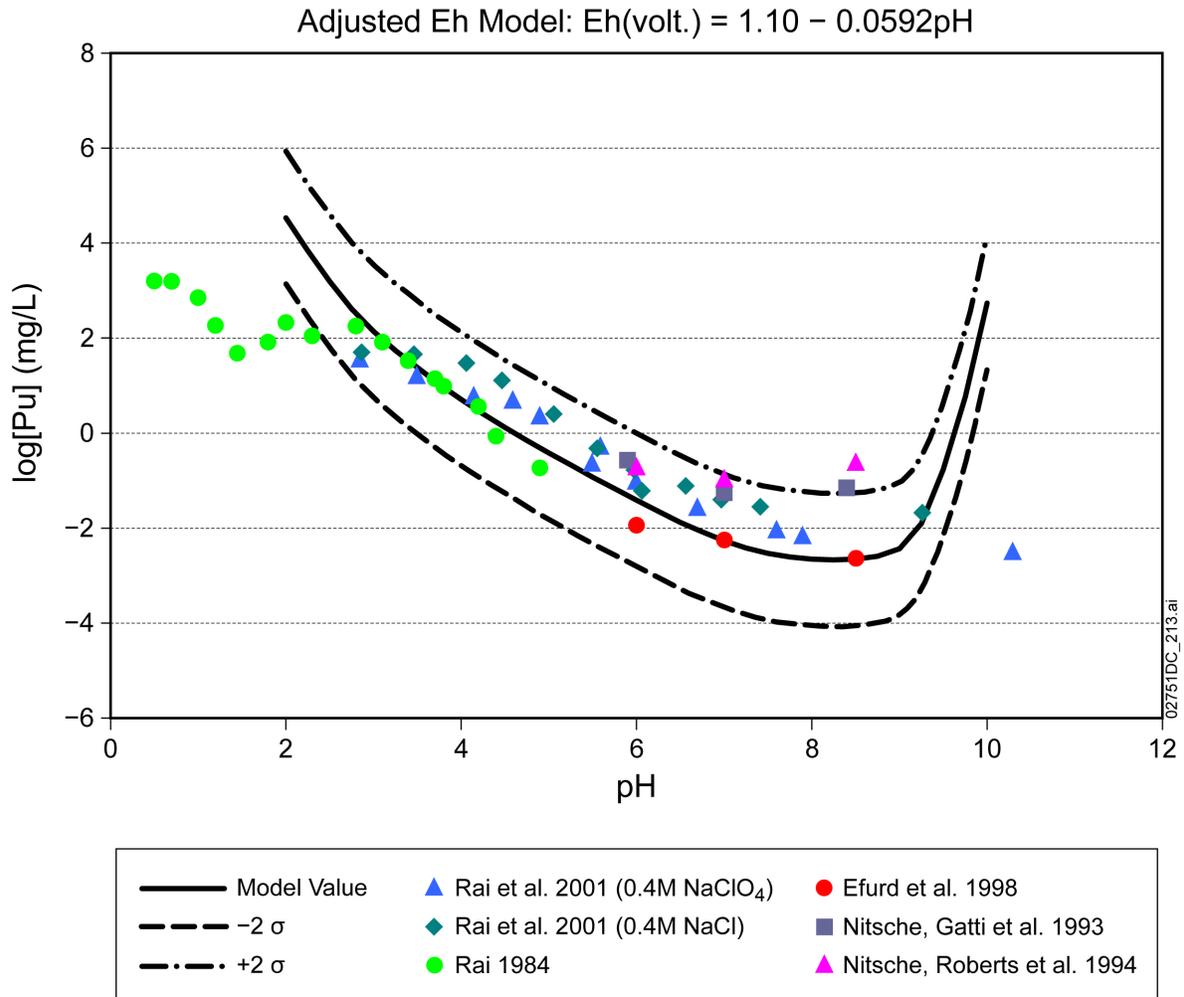


Figure 1 Comparison of Ambient Temperature Experimental Data to the Predicted Plutonium-Solubility Model Using Equation 1 to Calculate Eh



NOTE: This figure is the same as SAR Figure 2.3.7-37 but without the high-temperature experimental data. The Rai (2001) 0.4 M data are plotted as corrected pH, while the others including Rai (1984), which are in dilute solutions, are plotted as uncorrected pH.

Figure 2 Comparison of Ambient Temperature Experimental Data to the Predicted Plutonium-Solubility Model Using the Adjusted-Eh Solubility Model, Equation 2 to Calculate Eh

2. COMMITMENTS TO NRC

None.

3. DESCRIPTION OF PROPOSED LA CHANGE

None.

4. REFERENCES

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