DOC.20100125.0001

YMP	**Model** **Error Resolution Document** *Complete only applicable items.*	QA:QA Page 1 of 26

1. Document Number: ANL-WIS-MD-000010	2. Revision/Addendum: REV 06	3. ERD: 01

4. Title: Dissolved Concentration Limits of Elements with Radioactive Isotopes	5. No. of Pages Attached: 25

6. Description of and Justification for Change (Identify affected pages, applicable CRs and TBVs):

Description:

This Error Resolution Document (ERD) is generated to address CRs 12336, 13677, and 14113.

The major issue in CR 12336, "Lack of Information Regarding Data Sets Potentially Relevant to Modeling Limits on Dissolved Plutonium Concentrations for use in TSPA," is the choice of a Pu(IV) solubility-controlling solid instead of a Pu(VI) solid in the Pu dissolved concentration limits model. A new Appendix X addresses these and this ERD adds clarifying text. In addition, the CR attachment, *Additional Information CR 12336.pdf*, contains five other issues: 1) the use of higher temperature data, 2) the water chemistries in experiments and models, 3) the Eh of experiments and models, 4) the 10^{-6} mol/L threshold for colloid formation, and 5) isotopic correction for plutonium concentrations. These issues are also addressed in the new Appendix X. Issues 4 and 5 identify errors, which are corrected in this ERD. Issues 1 through 3 merit clarification text which is added in this ERD.

CRs 13677 "Incorrect Pu literature data illustrated on Figure and DTN" and 14113 "Pu log k uncertainty not updated in figures" identify two errors that are corrected in this ERD. Sections X.2 and X.3 discuss these errors.

Software Inputs Outputs:

Exempt Software (per IM-PRO-003, *Software Management*), Microsoft EXCEL 2007 SP-1 was used to evaluate these issues and to generate the revised figures and files in Output DTN: MO0707DISENSSI.000 and DTN: MO0707DISVALID.000. All other EXCEL files within these DTNS were generated using EXCEL 97 SR-2. Indirect inputs used in this ERD are added to Section 9.

List of Page Changes: See attached.

Documents Potentially Impacted: See attached.

Justification:

In the attached materials it has been determined that none of the corrections affect the conclusions of the original product and have no impact to the downstream work that has been performed. There is no impact to the conclusion of this report and this ERD sufficiently corrects the issues for the CRs 12336, 13677 and 14113 as detailed in the new Appendix X.

	Printed Name	Signature	Date
7. Checker	Susan E. Boggs		01/20/2010
8. QCS/QA Reviewer	Peter Persoff	Peter Persoff	01/20/2010
9. Originator	Christine Stockman	Christine Stockman	1/20/2010
10. Responsible Manager	Robert MacKinnon	Robert MacKinnon	1/20/2010

List of Page Changes:

Section-Page	**Figure/Text**	**CR 12336**	**CR 13677**	**CR 14113**	**Other**
5-1	Text	X			
6-50	Text	X			
6-51	Text	X			
6-56	Figure 6.5-6	X	X	X	
6-57	Text	X			
7-9	Figure 7-1 and text	X		X	
9	New references	X			
V-4	Figure V-2		X	X	
V-5	Text	X			
V-8	Text				X
V-12 and 13	Text				X
V-13	Figure V-8(a)		X	X	
V-13	Figure V-8(b)				X
V-14	Figure V-9		X	X	
X	New text	X	X	X	

See attached for page changes.

Impact Evaluation:

Controlled documents that cite ANL-WIS-MD-000010 REV 06 [DIRS 177418] include the following:

- ANL-EBS-GS-000001 Rev. 02, *Geochemistry Model Validation Report: Material Degradation and Release Model* [DIRS 181165]
- ANL-EBS-MD-000033 Rev. 06, *Engineered Barrier System: Physical and Chemical Environment* [DIRS 177412]
- ANL-EBS-MD-000037 Rev. 04, Add.01, *In-Package Chemistry Abstraction* [DIRS 180506]
- ANL-WIS-MD-000024 Rev. 01, *Postclosure Nuclear Safety Design Bases* [DIRS 177464]
- ANL-WIS-MD-000027 Rev. 00, *Features, Events, and Processes for the Total System Performance Assessment: Analyses* [DIRS 183041]
- ANL-WIS-PA-000001 Rev. 03, *EBS Radionuclide Transport Abstraction* [DIRS 177407]
- MDL-EBS-PA-000004 Rev. 03*, Waste Form and In-Drift Colloids- Associated Radionuclide Concentrations: Abstraction and Summary* [DIRS 177423]
- MDL-NBS-HS-000020 Rev. 02, Add. 01, *Particle Tracking Model and Abstraction of Transport Processes* [DIRS 181006]
- MDL-WIS-PA-000005 Rev. 00, Add. 01, *Total System Performance Assessment Model/Analysis for the License Application* [DIRS 183478]
- TDR-PCS-SE-000001 Rev. 05, Add. 01, *Performance Confirmation Plan* [DIRS 184797].

The documents listed above were searched for instances of “DIRS 177418.” The RAIs up to RAI 563 were searched for instances of “ANL-WIS-MD-000010.” In addition the SAR, FEIS and SEIS were searched. No impacts were found in the text; impacted figures are listed below. The impacted SAR figures will be processed using MGT-PRO-004, *Technical Work Activity Review Evaluation* and AP-REG-022, *License Application Configuration Management*.

For modified text listed above, there are no impacts to the output or conclusions of the parent document (SNL 2007 [DIRS 177418]). The added or modified text is for clarification only and does not change any conclusions. Therefore there are also no impacts to other documents except for the changed figures.

- Figure 6.5-6 is reproduced in RAI 258 as Figure 2 without the high temperature data.
- Figure 6.5-6 is reproduced in the SAR as Figure 2.3.7-37.
- Figure 7-1 is reproduced in the SAR as Figure 2.3.7-38.
- Figure V-2 is reproduced in the SAR as Figure 2.3.7-35.
- Figure V-8 is reproduced in RAI 258 as Figure 1.

Page Changes:

Page 5-1. Replace Section 5.1 with the following:

5.1 OXIDIZING CONDITIONS

Assumption: For modeling solubilities, the repository is assumed to be in an oxidizing condition. For most elements the oxygen fugacity is set equal to 0.2 bars (the atmospheric value). For neptunium and plutonium, conditions are more specific, as discussed in Sections 6.5 and 6.6.

Rationale: To simplify the modeling for elements with solubilities that are insensitive to fO_2, the fO_2 is set to 0.2 bars. It is also set to 0.2 bars for technetium, which results in there being no solubility limit for technetium. As the repository is in the unsaturated zone, it is connected to the atmosphere. Therefore, atmospheric oxygen fugacity is used. For plutonium phases and for some neptunium phases, solubilities are quite sensitive to fO_2, so for these, additional constraints are used that are more reducing. The existence of reducing conditions in the repository has not been proven, except for transient and localized conditions. However, within the waste packages, reducing conditions will occur locally as long as reductants such as steel and UO_2 are present, potentially hundreds of thousands of years after package breach.

Confirmation Status: Many of the radionuclides critical to dose are less soluble under reducing conditions (Langmuir 1997 [DIRS 100051], Chapter 13). Therefore, it is a conservative assumption because radionuclides are either more soluble under atmospheric oxygen fugacity or insensitive to oxygen fugacity. Thus, it does not need further confirmation.

Use in the Model: This assumption is used throughout Section 6, with an exception for Section 6.5 (plutonium-solubility model), and Section 6.6 (neptunium-solubility model), where slightly different redox conditions are used and a detailed rationale is given.

Page 6-28. Replace Section 6.4.2.1 with the following:

Oxidizing conditions are assumed (Section 5.1), and all solubility limits except neptunium and plutonium are calculated with a theoretical fO_2 of 0.2 bars (the atmospheric value). The details of the selection of the oxidation potential used in modeling plutonium and neptunium are discussed in Sections 6.5 and 6.6 and in Appendix V. A sensitivity study analyzing the effects of lower redox potentials on the solubility limits of neptunium, uranium, and technetium can be found in Appendix VIII.

Page 6-42. Replace first two sentences of 6.4.3.1 with:

This model uses fO_2 set to 0.2 bars for all elements except neptunium and plutonium.

Page 6-50 to 51. Replace last paragraph on p. 6-50 and first paragraph on p. 6-51 with the following:

Aging has been widely observed in plutonium precipitates or polymers in solubility experiments. For example, Rai and Ryan (1982 [DIRS 112060]) observed $PuO_2 \cdot xH_2O$ (amorphous) continuously aging over a period of 1,266 days by dehydration. The dehydration process of Pu(IV) hydrous involves the conversion of hydroxy bridge into oxygen bridge (Choppin 1983 [DIRS 168395]). This aging process is irreversible (i.e., once aged, the solid becomes kinetically stable (Choppin 2003 [DIRS 168308]) and difficult to redissolve). As stated by Rai (1984 [DIRS 122768]), "Although thermodynamic considerations dictate that the PuO_2:xH_2O(am) will eventually convert to PuO_2(c), Rai and Ryan (1982 [DIRS 112060]) have shown that radiolytic effects oppose the crystallization process, causing the crystallinity of the equilibrium solid phase to be somewhere between PuO_2:xH_2O(am) and the PuO_2(c), depending on the radiation field." For the high-radiation field provided by $^{238}PuO_2$, the Organization for Economic Co-operation and Development (OECD) (2001 [DIRS 159027], Section 17.2.2.3) notes that $^{238}PuO_2$(c) is converted to the amorphous solid in water. With the lower radiation field from $^{239}PuO_2$, $^{239}PuO_2$(c) is slowly converted to (or becomes coated with) a less-crystalline form when in contact with water. In the repository, the radiation fields will be high at emplacement, but by the time water returns to the drifts and the waste packages breach, the short-lived isotopes will be decayed away. This leaves the intermediate and long-lived isotopes such as ^{239}Pu and ^{238}U to dominate the radiation field, allowing the crystallinity of PuO_2(hyd,aged) to increase.

Page 6-51. Add to Section 6.5.3.1 before last paragraph:

Although this document uses $PuO_{2(hyd,aged)}$ as the solubility-controlling phase for plutonium, (SNL 2007 [DIRS 180506], Table 6-9[a]) cites the formation of the solid $PuO_2(OH)_2$:H_2O in calculations completed in that modeling effort. This mineral phase is discussed by several authors including Kim et al. (1984 [DIRS 123597]), Pashalidis et al. (1993 [DIRS 185840]), and Pashalidis et al. (1995 [DIRS 185841]). The constants for $PuO_2(OH)_2$:$2H_2O$ in the *data0.ymp.R2* database were derived from data documented by Pashalidis et al. (1995 [DIRS 185841]), but used the incorrect stoichiometry ($PuO_2(OH)_2$:$2H_2O$ instead of $PuO_2(OH)_2$:H_2O). The stoichiometry was corrected in the *data0.ymp.R5* database used by *In-Package Chemistry Abstraction* (SNL 2007 [DIRS 180506]) and SNL 2007 [DIRS 181165]), and this monohydrate was calculated to form under some conditions modeled in those documents. In both these documents fO_2 was assumed to be 0.2 bars and crystalline PuO_2 was suppressed. *In-Package Chemistry Abstraction* (SNL 2007 [DIRS 181165], p. 6-30), explained why $PuO_2(OH)_2$:H_2O was suppressed in its analysis (note, SNL 2007 [DIRS 181165] meant $PuO_2(OH)_2$:H_2O when it used $PuO_2(OH)_2$:$2H_2O$):

> EQ6 simulations at 50°C and 0.2 bars fO_2 showed $PuO_2(OH)_2$:$2H_2O$ to be marginally more stable than PuO_2(hyd,aged). Neither PuO_2(hyd, aged) nor $PuO_2(OH)_2$:$2H_2O$ have temperature coefficients in the *data0.ymp.R5* database (DTN: SN0612T0502404.014 [DIRS 178850]) However, the identity of $PuO_2(OH)_2$:$2H_2O$ has never been confirmed, and the logK (25°C) is given an uncertainty of 1 logK unit (Section 17.2.2.1 of *Chemical Thermodynamics of Neptunium and Plutonium* (OECD 2001 [DIRS 159027])). Furthermore, PuO_2(hyd, aged) is thought to become more stable (less soluble) with temperature (Efurd et al. 1998 [DIRS 108015]). Therefore, $PuO_2(OH)_2$:$2H_2O$ is suppressed.

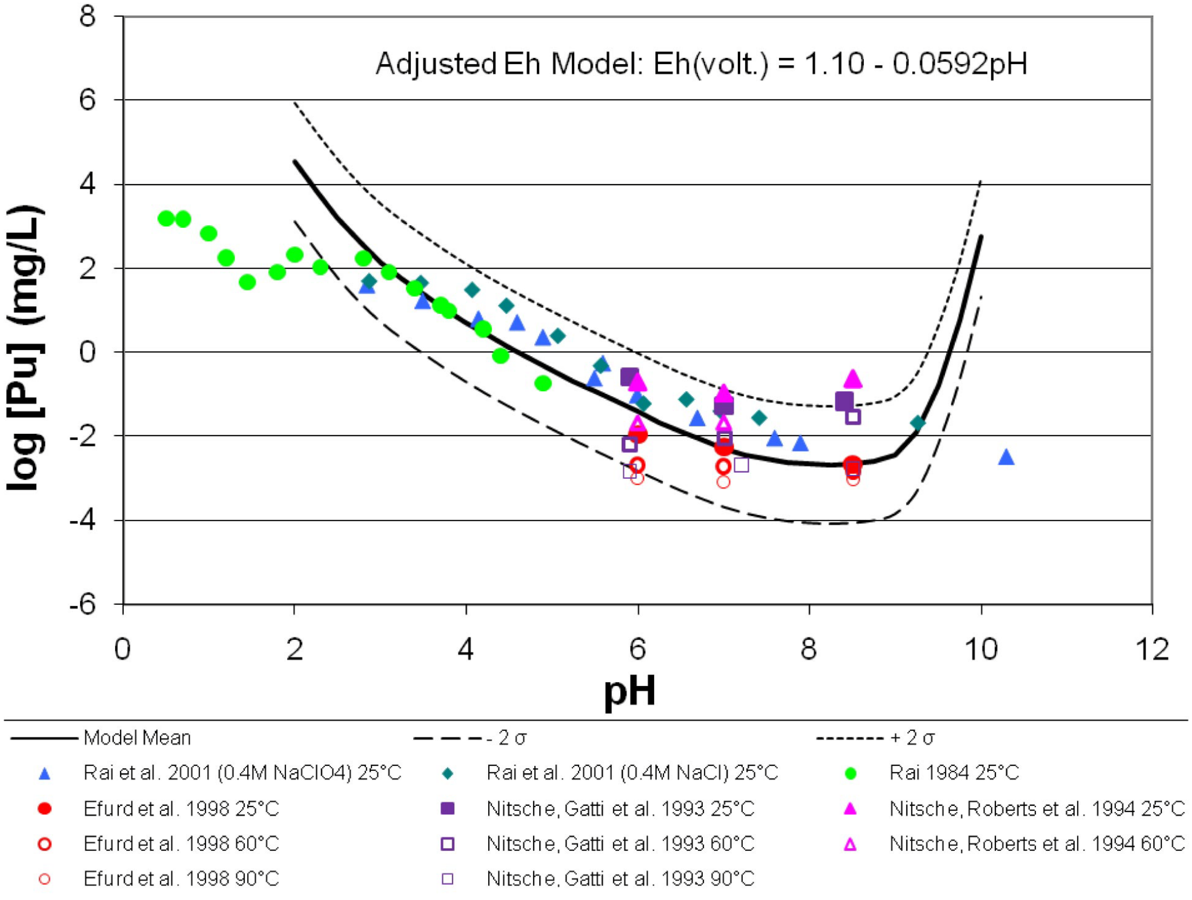
The intended uses of outputs from *In-Package Chemistry Abstraction* (SNL 2007 [DIRS 180506]) and from this model report in the LA are different. The plutonium solid allowed to form in *In-Package Chemistry Abstraction* (SNL 2007 [DIRS 180506]) will not affect the major outputs of the model used in the LA (pH and ionic strength), especially since plutonium is a minor component of a chemistry dominated by iron (Fe) and uranium (U). Under the conditions of fO_2 =

0.2 bar (SNL 2007 [DIRS 180506]), $PuO_2(OH)_2{:}H_2O$ and PuO_2(am,hyd) have similar stability given the uncertainty of the data; but with the adjusted Eh model used here, $PuO_2(OH)_2{:}H_2O$ is less stable and not a controlling phase.

Page 6-51. Replace first paragraph of Section 6.5.3.2 with:

The adjusted Eh model sets Eh conditions using Equation V-5, as described in Appendix V. Table 6.4-2 provides additional model calculation conditions. As indicated in Sections 6.3.3.3, 6.4.2.2, and 6.5.3.1, several conservatisms were used in the plutonium solubility model, namely the use of a hydrated, aged controlling phase and the use of a 25°C model for 25°C to 100°C. However, unlike other solubility models that report conservative upper bounds, the plutonium model presents a more realistic but still bounding estimate of the plutonium solubility for PuO_2(am,hyd) at 25°C (see Appendix V for details).

Page 6-56. Replace Figure 6.5-6 with the following:



Source: Output DTN: MO0707DISVALID.000, workbook: *Pu model-lab.xls,* sheet: *temperature on chart.*

NOTES: Modeled results are for log fCO_2 = –3.5. Rai 0.4M data is plotted by pc_{H}^{+}, while the others, which are dilute, are plotted as uncorrected pH.

Figure 6.5-6. Comparison of Experimental Data with the Predictions of the Plutonium-Solubility Model

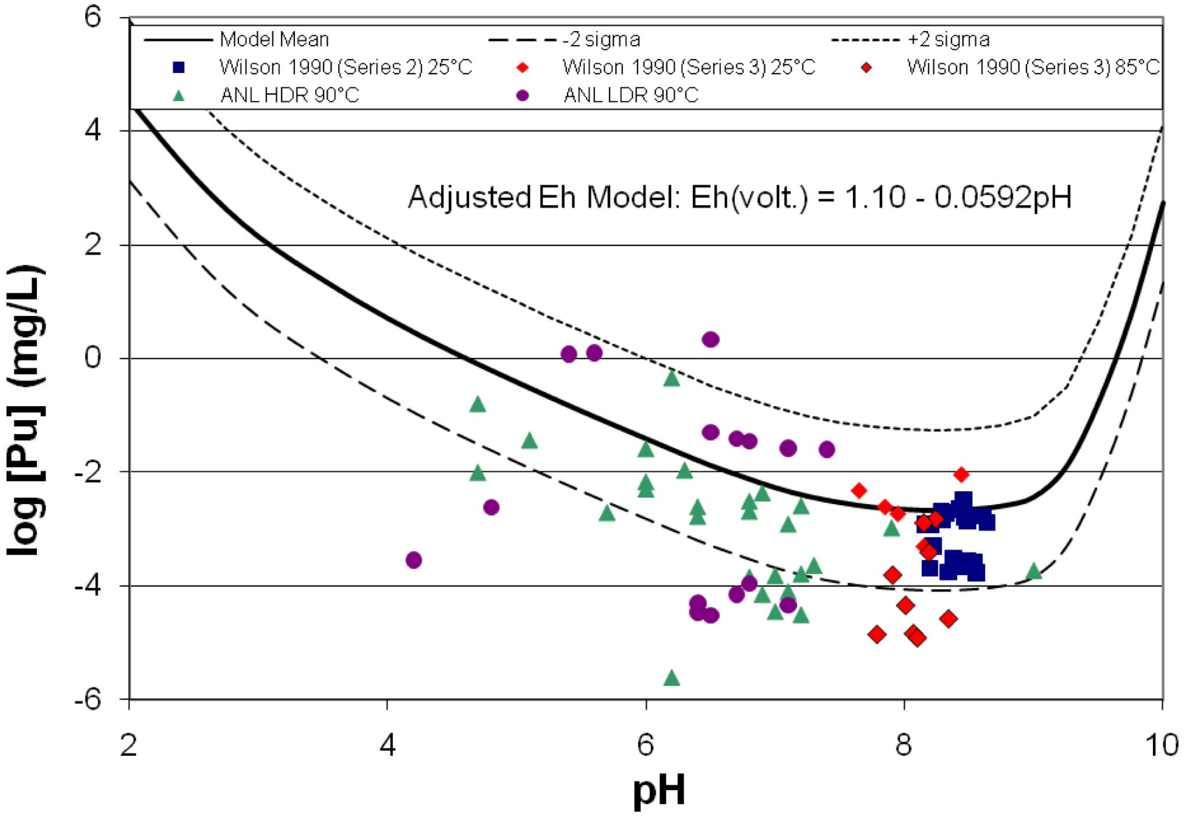
Page 6-57. In Section 6.5.3.3, replace the first paragraph on p. 6-57 with the following two paragraphs:

Experiments conducted by Rai (1984 [DIRS 122768]) and Rai et al. (2001 [DIRS 168392]) were open to air, while experiments conducted by Nitsche et al. (1993 [DIRS 155218]; Nitsche et al. 1994 [DIRS 144515]) and Efurd et al. (1998 [DIRS 108015]) were conducted in argon/CO_2 atmospheres of various CO_2 proportions. Nitsche et al. (1993 [DIRS 155218]) started with pure ^{239}Pu(IV) solutions, and reflect lower than atmospheric oxidation control as shown in the measured Eh values. However, the oxidation state conditions of those solutions are still considered relatively oxidizing, falling into the lower end of the range of meteoric waters, and into the range of natural groundwater, including rivers and lakes. The decrease in Eh (below atmospheric oxygen fugacity) in natural waters in contact with air is commonly due to reactions with reduced materials, which is very similar to the situation expected in the repository environment. The results from Nitsche et al. (1993 [DIRS 155218]; 1994 [DIRS 144515]) and Efurd et al. (1998 [DIRS 108015]) are reasonably consistent with the open to air results of Rai et al. (1984 [DIRS 122768]; 2001 [DIRS 168392]), especially compared to the uncertainty in the developed model.

Four different types of solutions were used in the experiments conducted by Rai et al. (2001 [DIRS 168392]): (1) 0.403 molal NaCl solution, (2) 0.408 molal $NaClO_4$ solution, (3) 4.36 molal NaCl solution, and (4) 4.92 molal $NaClO_4$ solution. Since the thermodynamic database used in this report is qualified for use for solutions having ionic strength less than 1.0 M, only the results of types (1) and (2) solutions reported by Rai et al. (2001 [DIRS 168392]) are discussed in this report. The solutions were filtered before measuring plutonium concentration in order to remove colloids. Table 6.5-2 lists the calculated pore sizes of filters (1.8 and 4.1 nm) used for filtration. Colloids are defined as particles with at least one dimension between 1 nm to 1 μm (Stumm and Morgan [DIRS 125332]). Nitsche et al. (1993 [DIRS 155218]; 1994 [DIRS 144515]) reported in their 25°C experiments that plutonium colloids consist of only 3% to 5% of total plutonium in the solution. Therefore, the measured plutonium solubility is considered as true dissolved plutonium concentration (since only a small amount of plutonium will be in colloidal form).

Page 7-9. Delete the last sentence of paragraph 1 and last sentence of paragraph 2.

Page 7-9. Replace Figure 7-1 with the following:



Data Source: Wilson 1990 [DIRS 100949]; 1990 [DIRS 100793] (Series 2 and Series 3 tests, respectively); CRWMS M&O 2000 [DIRS 131861]; 2000 [DIRS 153105] for Argonne National Laboratory (ANL) high-drip (HDR) and low-drip (LDR) tests.

Source: Validation DTN: MO0707DISENSSI.000, spreadsheet: *Wilson-ANL.xls*.

Figure 7-1. Comparison of Experimental Data with the Predictions of the Plutonium-Solubility Model at log $fCO_2 = -3.5$

Section 9. Add the following references to Section 9.1:

123597 Kim, J.I.; Bernkopf, M.; Lierse, C.; and Koppold, F. 1984. "Hydrolysis Reactions of AM(III) and Pu(IV) Ions in Near-Neutral Solutions." *Geochemical Behavior of Disposed Radioactive Waste.* Barney, G.S.; Navratil, J.D.; and Schulz, W.W., eds. ACS Symposium Series 246. Pages 115-134. Washington, D.C.: American Chemical Society. TIC: 219102.

185840 Pashalidis, I.; Runde, W.; and Kim, J.I. 1993. "A Study of Solid-Liquid Phase Equilibria of Pu(VI) and U(VI) in Aqueous Carbonate Systems." *Radiochimica Acta, 61,* 141-146. München, Germany: R. Oldenbourg Verlag. TIC: 260216.

185841 Pashalidis, I.; Kim, J.I.; Ashida, T; and Grenthe, I. 1995. "Spectroscopic Study of the Hydrolysis of PuO {subscript 2}{superscript 2+} in Aqueous Solution." *Radiochimica Acta, 68,* 99-104. München, Germany: R. Oldenbourg Verlag. TIC: 238486.

186525 Reed, D.T.; Lucchini, J.F.; Aase, S.B. and Kropf, A.J. 2006. "Reduction of Plutonium (VI) in Brine under Subsurface Conditions." *Radiochim Acta, 94,* 591 - 597. Munich, Germany: Oldenbourg Verlag. ACC: LLR.20091210.0020.

181165 SNL 2007. *Geochemistry Model Validation Report: Material Degradation and Release Model.* ANL-EBS-GS-000001 REV 02. Las Vegas, Nevada: Sandia National Laboratories. ACC: DOC.20070928.0010.

Section 9. Add the following reference to Section 9.3:

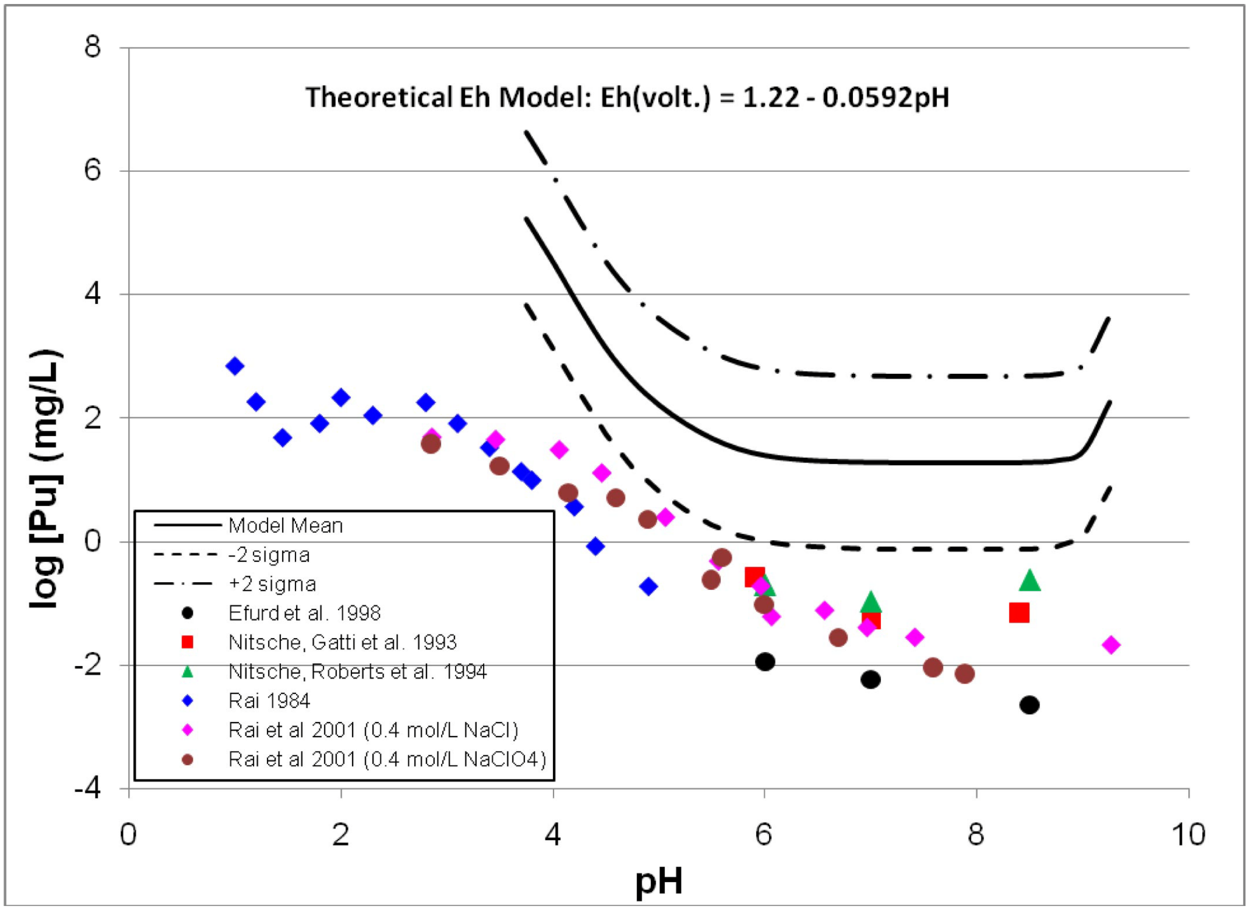
186332 SN0703PAEBSRTA.002. Surface Complexation Modeling Results, Actinide Kd Abstractions and pH Abstraction. Submittal date: 08/31/2009.

Section 9. Replace the following references in Section 9.4:

MO0707DISVALID.000. Dissolved Concentration Limits Files for Validated Models. Submittal date: 10/13/09.

MO0707DISENSSI.000. Dissolved Concentration Limits Files for Sensitivities and Validation. Submittal date: 10/13/09.

Page V-4. Replace Figure V-2 with the following:



Source: Validation DTN: MO0707DISENSSI.000, file: *pu solb 104-3.xls,* sheet *atmosphere compare.*

NOTES: Temperature = 25°C

Figure V-2. Comparison of the Theoretical (Atmospheric) Eh Plutonium Solubility Model with Plutonium Solubility Measurements

Page V-5. Replace the top paragraph with the following:

Some of the discrepancy between the model and data at low pH values is due to the effects of the sulfate that is in the model but not the experiments. (see Figure 6.4-3 and Section X.1.7.a.2 for the effects of sulfate on plutonium solubility.) However the poor match in Figure V-2 between the experiments and the theoretical fO_2 model is seen at all pH values, including neutral pH values where the effect of sulfate is minimal. The poor match at neutral pH values is not caused by sulfate and must be caused by something else. The inconsistency and the large difference between the experimental and modeling results strongly suggest that this model using a redox potential calculated from $fO2$ = 0.2 bars does not represent plutonium-solubility behavior.

Page V-8. Replace first paragraph with the following:

Other parameters used to represent redox conditions are Eh and pe (Eh = 0.0592pe at 25°C).

Assuming fO_2 = 0.2 bars is equivalent to assuming Equation V-1 (Wolery 1992 [DIRS 100836]; Krauskopf and Bird 1995 [DIRS 101702]; Langmuir 1997 [DIRS 100051]):

$$Eh(volt.) = 1.22 - 0.0592pH \qquad \text{(Eq. V-1)}$$

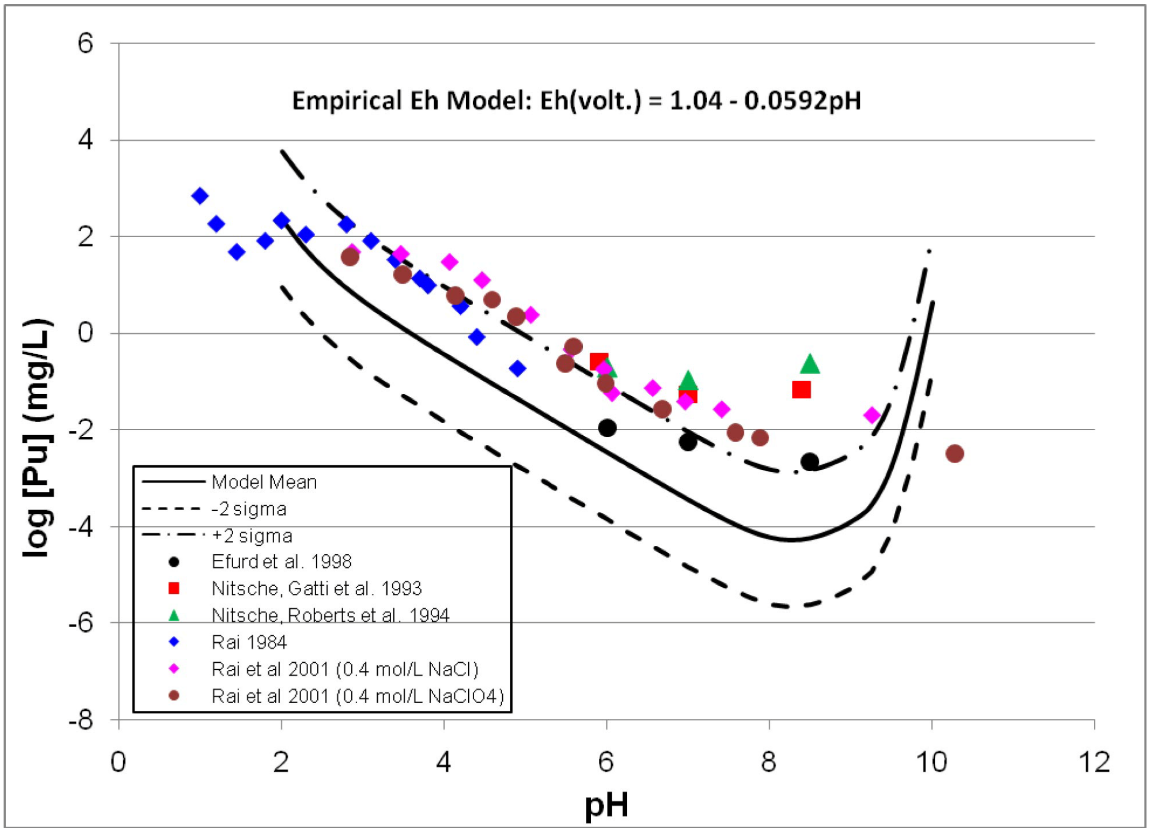
Equation V-1 is given by the Nernst equation for reaction:

$$2H_2O = O_2 + 4H^+ + 4e^- \qquad \text{(Eq. V-2)}$$

when fO_2 = 0.2 bars. This is the upper bound for natural waters shown on many Eh–pH diagrams.

Page V-12 and V-13. Replace references to “Figure V-8” with “Figure V-8a”, except for the middle of p. V-13 where it is replaced with “Figure V-8b”.

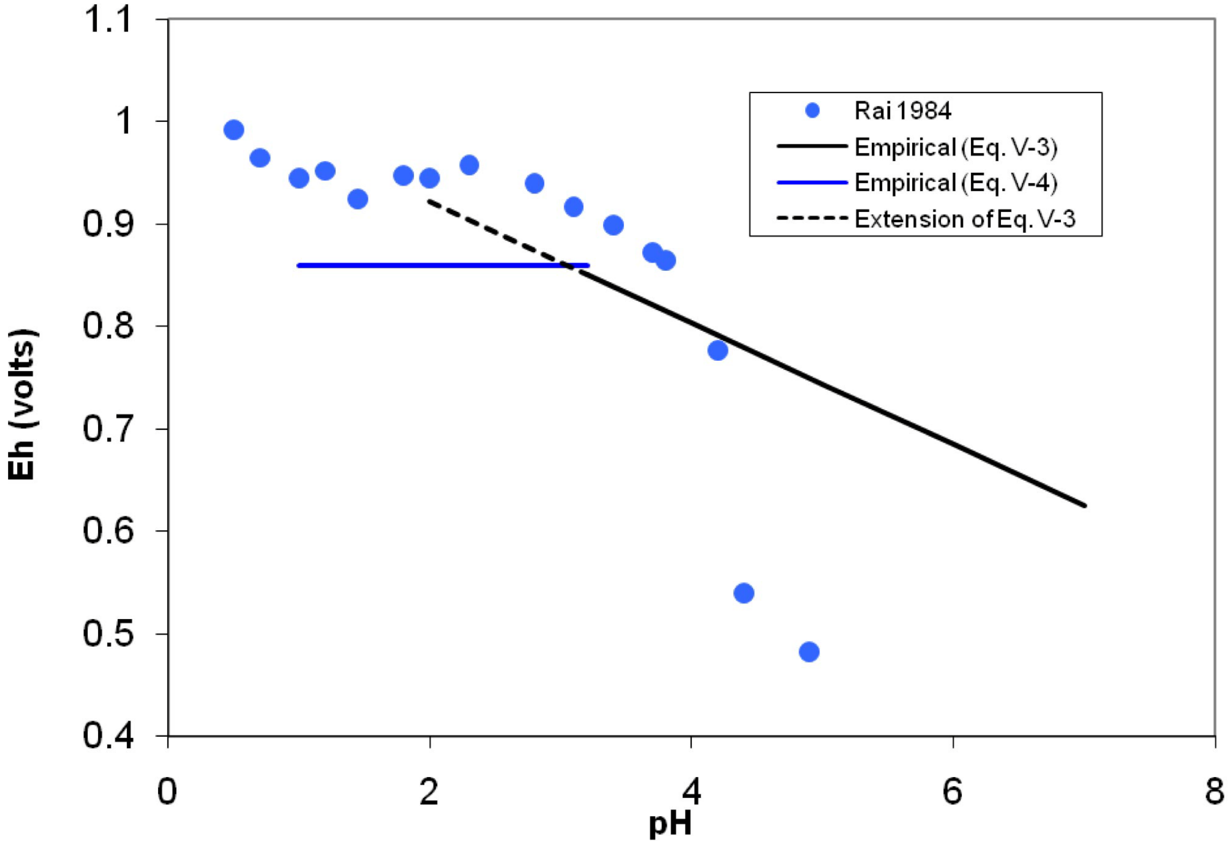
Page V-13. Replace Figure V-8 with the following Figures V-8a and V-8b.



Source: Validation DTN: MO0707DISENSSI.000, file: *pu solb 104-3.xls*, sheet: *empirical compare*.

NOTE: log fCO_2 = −3.5 bars, Temperature = 25°C

Figure V-8a. Comparison of the Empirical Eh Plutonium Solubility Model with Pu Solubility Measurements



Source: Validation DTN: MO0707DISENSSI.000, file: *pu solb 104-3.xls*, sheet *Eh.*

NOTE: log fCO_2 = −3.5 bars, Temperature = 25ºC.
Equation V-3 for pH > 3.2, Equation V-4 for pH <3.2.

Figure V-8b. Plutonium Empirical Eh Model

Page V-14. Replace Figure V-9 with same plot from the new Figure 6.5-6.

New Appendix X

Response to Issues Raised by CRs 12336, 13677, and 14113 on the Plutonium Dissolved Concentration Limits

Several technical issues with the plutonium dissolved concentration limits model were reported in CRs: 12336 "Lack of Information Regarding Data Sets Potentially Relevant to Modeling Limits on Dissolved Plutonium Concentrations for use in TSPA," 13677 "Incorrect Pu literature data illustrated on Figure and DTN," and 14113 "Pu log k uncertainty not updated in figures". Each issue is quoted, discussed, and the appropriate response implemented in ERD 01 to REV 06 of this document. The quoted text is italicized and indented. Text in blue are additions to this text, to help clarify and add transparency and traceability.

X.1 CR 12336 "LACK OF INFORMATION REGARDING DATA SETS POTENTIALLY RELEVANT TO MODELING LIMITS ON DISSOLVED PLUTONIUM CONCENTRATIONS FOR USE IN TSPA",

Issues from CR 12336 are contained in the condition description and attached file "*Additional Information CR 12336.pdf*. Preliminary responses to each paragraph in "Additional Information CR 12336.pdf" are given in CR attachment " preliminary responses to the CR attachment on Pu solid used etc.pdf". This appendix provides the final response to these issues. Subsection numbers within Section X.1 of this appendix indicate which item in the file *Additional Information CR 12336.pdf* is addressed in each subsection.

X.1.1.1 Condition Description and First Paragraph

The CR 12336 Condition Description states:

> *During review of open literature on plutonium solubility studies, several studies on the solubility of Pu(VI) solids were discovered. None of these studies is discussed or mentioned in the current version (nor any previous version) of the AMR, Limits on Dissolved Concentrations for Elements with Radioactive Isotopes (SNL 2007 [DIRS 177418]). Because they are not cited, it appears that these data were not evaluated or otherwise considered when developing the compliance model for calculating upper limits on dissolved concentrations for plutonium in repository waters. Consideration of these data sets could affect the basis for the current Pu-solubility model and therefore these data sets need to be considered to ensure that the current Pu-solubility model does not significantly under-estimate limits on dissolved plutonium concentrations for use in TSPA.*
>
> *This may be a condition adverse to quality. A detailed discussion of these experiments is required to determine whether (a) they are relevant to understanding limits on Pu concentrations in repository-relevant waters (and if so, the compliance model may need revision), or (b) they are irrelevant (and if so, the reasons for excluding them from further consideration must be adequately documented).*
>
> *See attachment ("Additional information CR12336") for more detailed information.*

First Paragraph of attachment:

> *Results of the Theoretical fO_2 model (which assumes equilibrium with the open atmosphere) for calculating plutonium concentrations in oxic water are shown in Sandia National Laboratory (*SNL*) 2007 (initiator referring to Dissolved Concentration Limits of Elements with Radioactive Isotopes [DIRS 177418]) to significantly over-predict experimentally measured plutonium concentrations from selected studies of PuO_2(am) solubility (Fig. V-2 of SNL 2007 [DIRS 177418]). Due to this discrepancy, the Theoretical fO_2 model was screened out and a new model, the Adjusted Eh model (the compliance model), was developed. The Adjusted Eh model predicts plutonium concentrations several orders of magnitude lower than the Theoretical fO_2 model and more closely matches the selected PuO_2(am) solubility data. However, the screening argument presented in the DCL [*dissolved concentration limits*] AMR (SNL 2007 [DIRS 177418]) does not contain a discussion of several potentially relevant plutonium(VI) solubility data sets. Those data do, in fact, agree reasonably well with both the trend and magnitude of plutonium concentrations predicted by the screened-out Theoretical fO_2 model, especially between pH 5 and 8.*

X.1.1.2 Response

The Pu(VI) solids alluded to in the condition description are specified in paragraph two of the attachment and are discussed in Section X.1.2.2. The plutonium-bearing solids (including $PuO_2(OH)_2{:}2H_2O$ and PuO_2CO_3) were not omitted from the thermodynamic database. They just were not chosen as solubility controlling solids. See Section 6.3.2 for discussion of the choice of the controlling solid. The detailed analysis of the relevance of the Pu(VI) solids and new literature data is ongoing using an updated database with the stoichiometric error in $PuO_2(OH)_2{:}2H_2O$ corrected to $PuO_2(OH)_2{:}H_2O$. If that analysis concludes that the Pu(VI) solids are relevant to the repository waters, then a revision of this document can be initiated.

X.1.2.1 Second Paragraph

> *The omitted data concern the solubility of plutonium-bearing solids (including $PuO_2(OH)_2{:}H_2O$ and PuO_2CO_3) that might form and help control dissolved plutonium concentrations in oxidizing waters (e.g., Kim et al. 1984 [DIRS 123597], Pashalidis et al. 1993 [DIRS 185840], Pashalidis et al. 1995 [DIRS 185841], among others noted in the NEA volumes. Most of these data sets are also discussed in both NEA volumes on plutonium thermodynamics cited by SNL 2007 [DIRS 177418] (Grenthe et al. 1992 [DIRS 101671] (should be OECD 2001 [DIRS 159027] as Grenthe et al. 1992 [DIRS 101671 is for uranium) and Guillaumont et al. 2003 [DIRS 168382]; see pages 317-321 of Vol. 4; cf. Fig. 17.1 of OECD 2001 [DIRS 159027]). It is not clear why there is no mention of these data in SNL 2007 [DIRS 177418] (or in any previous version of this AMR).*

X.1.2.2 Response

The plutonium-bearing solids (including $PuO_2(OH)_2{:}2H_2O$ and PuO_2CO_3) were not omitted from the thermodynamic database, although they were not chosen as solubility-controlling solids (see Section 6.3.2).

Within the spent fuel, plutonium is in the Pu(IV) oxidation state. When exposed to the air, the plutonium solid is expected to remain in the (IV) oxidation state, as the PuO_2(am) did in the Rai (1984 [DIRS 122768]) and Rai et al. (2001 [DIRS 168392]) experiments. This is especially true when reductants such as steel and UO_2 are present, as would be expected inside the waste packages for hundreds of thousands of years. Even after all reductants are oxidized, it is not expected that the Eh will rise to the level that would convert all plutonium to Pu(VI) as was done by Pashalidis et al. (1993 [DIRS 185840]) and Pashalidis et al. (1995 [DIRS 185841]), the latter of which were solubility studies specific for Pu(VI) solids, whereby strong oxidants were used to obtain pure Pu(VI). Because the waste packages and invert are expected to have fO_2 of 0.2 bars or lower, the focus of the discussion was on Pu(IV) solids.

This issue is similar to the issue discussed in Sections X.1.3.1 and X.1.3.2. See Section X.1.3.2 for a discussion of added text on p. 6-51.

X.1.3.1 Third paragraph

> *The omission of this data (or any discussion of the associated studies) is especially curious because the related AMR, In-Package Chemistry Abstraction (BSC 2005) (report now associated with an addendum, See SNL 2007 [DIRS 180506]) reports that the plutonium(VI) solid, $PuO_2(OH)_2:H_2O$, is the solubility-controlling solid for plutonium in modeling runs performed for in-package chemistry calculations (this mineral is not reported in BSC 2005). BSC 2005 asserts that this Pu(VI) solid "is a thermodynamically stable compound that would be expected to form from the degradation of CSNF" (Table 6-9 (Table 6-9 of BSC 2005 is incorrectly cited. Additionally, Table 6-11 does not report this phase in its list of mineral phases); also see 2007 IPC AMR Addendum (SNL 2007 [DIRS 180506]), Table 6-9[a]; p.6-17[a]). No discussion (either supporting or refuting) this assertion is provided in SNL (2007) [DIRS 177418].*

X.1.3.2 Response

In-Package Chemistry Abstraction (SNL 2007 [DIRS 180506]) allows the thermodynamic code to choose the minerals formed based on thermodynamic equilibria defined by species within the database. However the most stable Pu solid in the database, PuO_2 (cr), was suppressed and not allowed to precipitate for kinetic reasons. In another analysis, *Geochemistry Model Validation Report: Material Degradation and Release Model* (SNL 2007 [DIRS 181165]), using *Data0.ymp.R5*, the most recent version of the database, $PuO_2(OH)_2:H_2O$ was also suppressed as explained on p. 6-30 of that document and quoted on p. 6-51 here. Given the uncertainty of the thermodynamic stability data, and the fact that PuO_2(hyd, aged) stability is greater when further aged and more crystalline as with higher temperatures, PuO_2(am, aged) was chosen as the solubility controlling solid.

For clarification, text is added to p. 6-51 per this ERD.

X.1.4.1 Fourth Paragraph

> *In addition, the Pu(VI) concentration data in the studies omitted from SNL 2007 [DIRS 177418] contradict the contention in Section V.2.2 of SNL (2007 [DIRS 177418]) that dissolved Pu concentrations greater than 0.000001 moles per liter are unstable with respect to*

> *colloid formation, as no colloids are reported in the omitted studies. In fact, those (and more recent) studies report that considerably higher concentrations of dissolved Pu(VI) remain stable with respect to both precipitation and reduction for as long as two years (Fig. XX Initiator referring to Figure 4 in CR 12336, Attached File: Additional Information CR 12336.doc).*

X.1.4.2 Response

This paragraph identifies a misrepresentation of the Choppin (1983 [DIRS 168395]) work on page V-5. Text deleted on page V-5 per this ERD.

X.1.5.1 Fifth Paragraph

> *The omitted data sets agree rather well with the magnitude and trend of Pu concentrations calculated with the Theoretical fO_2 model that is screened out in Appendix V of SNL (2007) [DIRS 177418], which claims that plutonium concentrations predicted by that model are unrealistic. However, when compared against the omitted data sets, the Theoretical fO_2 model appears quite realistic, especially between about pH 5 and 8 (Fig. 6 ~~below~~ in CR 12336, Attached File: Additional Information CR 12336.doc).*

X.1.5.2 Response

Figure 4 of the condition report attachment shows the plutonium concentrations for solubility experiments for $PuO_2(OH)_2{:}H_2O$ and PuO_2CO_3. At or near atmospheric fCO_2, these data plot at 10 mg/L or higher, even between pH 6 and 8, which is consistent with the theoretical fCO_2 model. However, in these experiments, care was taken to convert all plutonium to Pu(VI) and to eliminate all kinetically-significant reductants from the system. These conditions are not expected within the repository, either within the waste package or within the invert.

TSPA requires the dissolved plutonium concentration limits for fluids within the waste package and invert during and after commercial SNF and steel degradation, and therefore the adjusted-Eh model is "more realistic" than the theoretical fO_2 model.

X.1.6.a.1 Sixth Paragraph (Item 1 and 1a)

> *Although the compliance model is calculated for 25°C with the explicit claim that dissolved concentrations at this temperature are conservative with respect to solubility-limited concentrations at higher temperatures (SNL 2007 [DIRS 177418], Section 6.4.2.2, find a more in depth discussion in 6.3.3.3), the use of data obtained from experiments conducted well above 25°C are compared against the 25°C model. These data are not clearly identified as corresponding to temperatures above 25°C.*
>
> a. *Figure 6.5-6 (p. 6-56) was altered between Revision 03 and Revision 04 of SNL 2007 [DIRS 177418], to include 60°C and 90°C data from solubility experiments conducted by Nitsche et al. (1993[DIRS 155218], 1994 [DIRS 144515]) and Efurd et al. (1998 [DIRS 108015]). These higher-temperature data are the only data to plot below the calculated model curve between pH 6 and 10, making the model appear more conservative than it is.*

X.1.6.a.2 Response

As discussed in *Dissolved Concentration Limits of Elements with Radioactive Isotopes* (SNL 2007 [DIRS 177418], Sections 6.3.3.3, 6.4.2.2, and 8.1.3; Table 6.4-2), the models are valid for 25°C to 100°C. Therefore, adding the higher temperature data is reasonable given the valid temperature range for the model. Figure 6.5-6 is replaced with a version that identifies the temperatures of the experiments per this ERD.

X.1.6.b Sixth Paragraph (Item 1b)

b. SNL 2007 [DIRS 177418], Figure 7-1 includes data obtained from CSNF corrosion experiments conducted at 85° (Wilson 1990 [DIRS 100949] and Wilson 1990 [DIRS 100793]) and 90°C (CRWMS M&O 2000a [DIRS 131861]; CRWMS M&O 2000b [DIRS 153105]) for comparison with plutonium concentrations based on the compliance model calculated for 25°C. In addition, data from Commercial Spent Nuclear Fuel Degradation in Unsaturated Drip Tests (CRWMS M&O 2000a [DIRS 131861) and Measured Solubilities, Argon National Lab High Drip Rate Tests (CRWMS M&O 2000b [DIRS 153105]) correspond to measurements of plutonium-239 only, which comprises only about 60% of total plutonium in those samples. Although the Wilson (1990 [DIRS 100949]; 1990 [DIRS 100793]) data were corrected for this isotopic effect before use of that data in SNL 2007 [DIRS 177418], no correction was made for the CRWMS M&O (2000 [DIRS 131861]; 2000 [DIRS 153105]) data. The combined errors for temperature (approximately 10 times) and isotope (roughly two times) is nearly 20 times, the data, if corrected, being more than an order of magnitude higher than the uncorrected data (see attachment).

X.1.6.b.2 Response

Correcting the data for temperature, as suggested, is not straight forward, because temperature has several effects. These include accelerated aging of amorphous solids to more crystalline solids at higher temperatures and lower carbonate concentrations at higher temperature, both of which would lower the dissolved plutonium concentration. Rather than "correcting" the data for temperature effects as suggested by the initiator, the temperatures for the data points are explicitly identified in the new Figure 7-1 to enhance clarity.

Reexamination of *Wilson-ANL.xls* from Output DTN: MO0707DISENSSI.000 (REV 01) shows that the data from *Commercial Spent Nuclear Fuel Degradation in Unsaturated Drip Tests* (CRWMS M&O 2000 [DIRS 131861]) and *Measured Solubilities, Argon National Lab High Drip Rate Tests* (CRWMS M&O 2000 [DIRS 153105]) was not corrected for isotopic versus total Pu in the system. Correcting this error changes Figure 7-1 slightly (see new Figure 7-1) but does not alter the conclusions. The updates to *Wilson-ANL.xls* used to create Figure 7-1 are presented in Rev 03 of DTN: MO0707DISENSSI.000.

X.1.6.i.1 Sixth Paragraph (Item i)

i. Although the experimental data as presented in Figure 7-1 (SNL 2007 [DIRS 177418]) may be too low by [an] order of magnitude or more compared to 25[°]C values, Numerous data

> *fall well above the predicted mean solubility limit for PuO_2(am) (to be consistent with SNL 2007 [DIRS 177418] this should be PuO_2(hyd,aged)). That is, "limits" on dissolved plutonium concentrations predicted by the compliance model fail to encompass plutonium concentrations observed in the CSNF corrosion experiments (whether corrected or uncorrected). This is contrary to the tenet that the dissolved concentration of an element in a waste form will be at or below its solubility limit, especially during waste-form dissolution.*

X.1.6.i.2 Response

When there is no solubility model uncertainty, then, in the absence of supersaturation, all relevant experimental concentrations should fall below the solubility model limit. However, in TSPA the solubility model is uncertain and represented with specified uncertainty. Thus TSPA provides the probability that the solubility will actually be at a certain value. Typically, it is the 2σ, or the 95th percentile of the solubility distribution that is used as the practical limit for comparison with experiments as was shown in Figure 7-1.

In practice, TSPA uses the sampled solubility limit as the dissolved concentration whenever there is excess of an element in a given location. Thus the term "dissolved concentration limit" was used instead of "solubility" in the title of this document. Within the waste form domain, degradation of the waste form usually provides an excess of plutonium at early times, and the dissolved concentration is set to the solubility limit. Because the modeled plutonium dissolved concentration is an important parameter to repository performance, the project chose to represent this parameter in a "more realistic way" instead of using "overly bounding approximations." An empirical dissolved concentration model would have provided the distribution of data from relevant experiments such as those in Figure 7-1, and would have had a lower mean and wider distribution than the adjusted Eh model. Thus the adjusted Eh model is "somewhat bounding."

X.1.6.1.1 Sixth Paragraph Last Subsection

> *Solubility and other Pu concentration data obtained from experiments conducted at temperatures well above 25°C and used for comparison with dissolved Pu concentrations calculated for 25[°]C should be either eliminated from all figures or corrected for estimated temperature effects and clearly labeled. Pu concentration data reported from CSNF corrosion studies must be corrected for isotopic bias, as was done for data from Wilson (1990 [DIRS 100949]; 1990 [DIRS 100793]).*

X.1.6.1.2 Response

Because the relative importance of crystallinity versus other factors at higher temperature is uncertain, and aging to more crystalline solids is irreversible (Choppin 2003 [DIRS 168308]), it is dubious to "correct" the data for temperature effects without further experimental evidence. The temperatures of the experiments are identified on the Figures 6.5-6 and 7-1 in this ERD. Isotopic bias has been corrected per this ERD. See pp. 6-50 to 6-51 rewrite for clarifying text.

X.1.7.a.1 Seventh Paragraph (Item 2a)

> *The chemistry used as input to both the screened-out model (Theoretical fO_2 model) and the*

compliance model (Adjusted Eh model) differ from the chemistry of the experiments the models are evaluated against and then used to represent (Table 1 in CR 12336, Attached File: Additional Information CR 12336.doc).

a. The chemistry of water modeled in the Theoretical fO_2 model imposed high levels of dissolved sulfate in acid waters (pH less than about 6), with dissolved sulfate exceeding 2 molar at pH 3.5. Sulfate, a strong complexant of dissolved Pu(VI), was not present in any of the experiments being modeled.

X.1.7.a.2 Response

The effect of sulfate on the adjusted-Eh plutonium concentrations was investigated in Section 6.4.2.5.1 Figure 6.4-3, p. 6-33. Sulfate has no effect at neutral pH but has some effect at very high and very low pH. Sulfate has more effect on plutonium concentration at low pH with the theoretical fO_2 model than with the adjusted-Eh model due to the greater importance of $PuO_2SO_4(aq)$ at the higher Eh. For example, with the case mentioned above, with $\log fO_2 = -0.7$, $\log fCO_2 = -3.0$, and $pH = 3.5$, 72% of the dissolved plutonium is due to plutonyl sulfate complexes (DTN: MO0707DISENSSI.000, *MWD for sens and val rev 2.zip*, file: MWD for sens and val\Pu\25C\cases for Eh adjustment\atm O2\SO4*pu010403.3o*) At that pH, $[SO_4^{2-}]$ = 0.06 molal, $[PuO_2SO_4(aq)]$ = 1.1 molal, $[PuO_2(SO_4)_2^{2-}]$ = 0.55 molal, $[PuO_2^{2+}]$ =0.6 molal, and total aqueous sulfate = 2.23 molar. Thus the dissolved sulfate exceeding 2 molar at pH 3.5 is not due to SO_4^{2-}, but plutonyl sulfate complexes, and the sulfate is about 300 times the J-13 value of 18.4 mg/L (2×10^{-4} mol/L).

The poor match in Figure V-2 between the experiments and the theoretical fO_2 model is seen at all pH values, including neutral pH values where the effect of sulfate is minimal. For example at $\log fO_2 = -0.7$, $\log fCO_2 = -3.0$, and $pH = 6$, $PuO_2SO_4(aq)$ is responsible for only 0.5% of the dissolved plutonium concentration which is dominated by $PuO_2CO_3(aq)$ (DTN: MO0707DISENSSI.000, *MWD for sens and val rev 2.zip*, file: MWD for sens and val\Pu\25C\cases for Eh adjustment\atm O2\SO4*pu010403.3o*). Thus the poor match at pH 6 is not caused by sulfate. Some of this sulfate discussion is added to the last paragraph of Section V.2.2 on p. V-5 of this ERD.

X.1.7.b.1 Seventh Paragraph (Item 2b)

b. Groundwater constituents were used as model input when attempting to model experiments that had not been conducted with groundwater (Rai 1984 [DIRS 122768], Rai et al. 2001 [DIRS 168392]).

X.1.7.b.2 Response

Section 6.4.2.5.1 investigates the effects of varying ligand concentrations on actinide solubilities. The groundwater constituent comparison is important to demonstrate that the model appropriately predicts dissolved concentration limits for plutonium under varying ligand concentrations. As shown in this section, even significantly higher concentration of most groundwater constituents have no influence on dissolved actinide concentrations. Those that do have a significant effect on actinide aqueous concentrations are either built into the model or are added as an uncertainty parameter. Dilute solutions produce comparable results (SNL 2007 [DIRS 177418], Section

6.4.2.5.1). Also, this analysis is not trying to recreate the laboratory results perfectly (that would be an EQ3/6 validation/qualification effort). Instead, an assessment of actinide concentrations in Yucca Mountain waters is conducted. However, as discussed previously, dilute solutions give similar results. Therefore, there is no impact on the comparison of laboratory results obtained with simple water compositions versus modeling using groundwater containing constituents not in the experiments.

X.1.7.c.1 Seventh Paragraph (Item 2c)

> *c. The screened-out Theoretical fO_2 model and the Adjusted Eh model were both compared with experiments that included studies performed under anoxic conditions (i.e., Ar atmospheres: Nitsche et al. 1993 [DIRS 155218], 1994 [DIRS 144515]); Efurd et al. 1998 [DIRS 108015]), conditions not assumed to persist in the repository according to Section 5.1 of SNL (2007) [DIRS 177418]. No discussion is provided in SNL 2007 [DIRS 177418] as to why PuO_2(am) solubility data obtained under anoxic conditions would have been expected to resemble estimates of Pu solubilities under atmospheric oxygen fugacity (Theoretical model), despite the assertion in Section 6.4.1 of SNL (2007) [DIRS 177418] that oxidation potential has the strongest single effect on the solubility of the actinides (except Th and Am).*

X.1.7.c.2 Response

The assumption in Section 5.1 is reworded to clarify that neptunium and plutonium use a less bounding assumption, and that less than atmospheric redox conditions are expected within the waste packages for hundreds of thousands of years.

The comparison of the model with the data from Nitsche et al. (1993 [DIRS 155218], 1994 [DIRS 144515]) and Efurd et al. (1998 [DIRS 108015]) is discussed explicitly (SNL 2007 [DIRS 177418], Section 6.5.3.3, Figure 6.5-6) and the gas conditions in those experiments stated clearly (SNL 2007 [DIRS 177418], top of p. 6-57). In that figure, these data are also compared with those from Rai et al. (1984 DIRS 122768], 2001 [DIRS 168392]) that were conducted open to air. The open to air results of Rai et al. (1984 DIRS 122768], 2001 [DIRS 168392]) are reasonably consistent with the Nitsche et al. (1993 [DIRS 155218], 1994 [DIRS 144515]) and Efurd et al. (1998 [DIRS 108015]) results, especially compared to the uncertainty in the model as developed. The Nitsche et al. (1993 [DIRS 155218], 1994 [DIRS 144515]) studies started with pure ^{239}Pu(IV) solutions and reflect lower oxidation control as shown in the measured Eh values, likely due to the Ar/CO_2 atmosphere, as well as the reaction with tetravalent plutonium. However, as discussed by Nitsche et al. (1993 [DIRS 155218]) and shown by the measured Eh values reported therein, the oxidation state conditions of those solutions are still considered relatively oxidizing, falling into the lower end of the range of meteoric waters, and into the range of natural groundwater, including rivers and lakes. The decrease in Eh (below atmospheric oxygen fugacity) in natural waters in contact with air is commonly due to reactions with reduced materials, which is very similar to the situation expected in the repository environment. *Dissolved Concentration Limits of Elements with Radioactive Isotopes* (SNL 2007 [DIRS 177418], Appendix V) discusses the relevance of experimental redox conditions in detail, by comparing the experimental solubility data sets to calculated dissolved plutonium concentrations of PuO_2(hyd,aged) in equilibrium with air (the theoretical fCO_2 model) (SNL 2007 [DIRS 177418], Figure V-2). The discussion of the discrepancy between those measured values and the calculations focuses on the resulting speciation in the atmospheric oxygen calculations being inconsistent with: (a) the observed speciation in the experimental results, (b) the speciation observed for Pu in some natural waters, and (c) the plutonium solubility model speciation. This discussion acknowledges that the oxidation state plays a large role in plutonium behavior. The conclusion is that, based on the plutonium speciation (even in natural waters), the adjusted Eh model is the more appropriate representation compared to the conservative assumption of using atmospheric oxygen fugacity.

See reworded p. 6-57 as part of this ERD.

X.1.8.1 Eighth Paragraph

> *Sections 6.3.2 and 6.5.3.1 of SNL (2007 [DIRS 177418]), which describe the selection of solubility-limiting solid for controlling Pu concentrations, needs to either (1) justify why Pu(VI) solids should be excluded from consideration given that these solids appear to have solubilities quite similar to those predicted by the Theoretical fO_2 model for PuO_2(am) under assumed repository-relevant conditions (as stated in Section 5.1 of SNL 2007 [DIRS 177418]), or (2) revise the model to include the potential influence of Pu(VI) solids on dissolved Pu concentrations.*

X.1.8.2 Response

Assumption 5.1 is reworded to avoid the confusion as to repository-relevant redox conditions. A detailed analysis of the relevance of the Pu(VI) solids and new literature data is ongoing. If that analysis concludes that the Pu(VI) solids are relevant to the repository waters, then a revision of this document can be initiated.

X.1.9.1 Section 1.1 Solubility Studies of $PuO_2(OH)\cdot H_2O$ paragraph 1

> *As noted above, the selection of data against which to compare model results is crucial for defending the model results as being representative of expected repository-relevant behavior. The overriding assumption that the repository is expected to be oxidizing (constant fO_2 = 0.2 bar) dictates that Pu concentration limits be modeled by assuming such oxidizing conditions. This was done by using the "Theoretical fO_2" model for Pu solubility, and Figure V-2 of SNL (2007) compares the results of the "Theoretical fO_2" model (calculated by assuming log fCO_2 = 3.5) with data from the six selected PuO_2(am) solubility data sets (Rai 1984 DIRS 122768], Rai et al. 2001 [DIRS 168392]), Nitsche et al. 1993 [DIRS 155218], Nitsche et al. 1994 [DIRS 144515]), Efurd et al. 1998 [DIRS 108015]). The agreement is correctly noted to be very poor, with model results exceeding data by two or more orders of magnitude between pH 4 and 9. This poor agreement between model and data is the reason that the "Theoretical fO_2" model is screened out, providing the motivating rationale for developing the "Adjusted Eh" model. However, solubility data from the studies on Pu(VI) solubility not addressed in SNL (2007) are shown in below (Figure 4 of Additional information CR12336.pdf)), which compares these data against results of the "Theoretical fO_2" model (log fCO_2 = −3.5 and −5.0) calculated for PuO_2(am) solubility. It is clear that between pH of about 5 and 8, the agreement is actually quite reasonable, contrary to the contention in SNL (2007) that Pu concentrations predicted by the "Theoretical fO_2" model are "unrealistic" (p. V-5).*

X.1.9.2 Response

The agreement between the theoretical fO_2 model and the Pu(VI) solubility experiments is expected, because Pu(VI) species are dominant in both. However, the redox conditions of these experiments and theoretical model are higher than that expected within the repository.

As noted above, the assumption of oxidizing conditions is a modeling decision used to simplify the modeling of elements that are insensitive to redox conditions. The assumption of $fO_2 = 0.2$ bar is not made for plutonium. Assumption 5.1 on p. 5-1 is reworded to clarify this point.

The solubility data sets of Rai (1984 [DIRS 122768]) and Rai et al. (2001 [DIRS 168392]) are deemed most applicable to repository conditions because PuO_2 experiments open to the air are similar to commercial SNF or HLW degradation in waste packages open to the air. The actual environments within the waste packages are not in equilibrium for hundreds of thousands of years, rather they will have an fO_2 gradient between the outside of the package and the reducing materials (commercial SNF, HLW and steel) within the package as shown in Figure IV-2. The concentration limit of plutonium in the waters that exit the waste package is most important to TSPA. The Rai (1984 [DIRS 122768]) and Rai et al. (2001 [DIRS 168392]) experiments most closely approximate this.

X.1.10.1 Solubility Studies of $PuO_2(OH)·H_2O$ paragraph 2

> *As noted above, the assertion (SNL 2007 [DIRS 177418], section V.2.1, p. V-5) that concentrations of plutonium greater than* 10^{-6} *mol/L [approx 0.24 mg/L] are unstable relative to Pu(IV) colloid formation is not supported by experimental evidence, at least for oxidizing conditions (such as those assumed to exist in the repository). The study by Kim et al. (1984 [DIRS 123597]) demonstrated that dissolved concentrations of Pu(VI) remained stable in solutions equilibrated with* $PuO_2(OH)_2·H_2O$ *for "several weeks." Pashalidis et al. (1995 [DIRS 185841]) demonstrated that 0.01 M Pu(VI) (2,390 mg/L) remained stable with respect to reduction and precipitation for five months in 0.1 M* $NaClO_4/NaOH$ *solutions (pH 7). More recently, Reed et al. (2006 [DIRS 186525]) demonstrated that, in simulated WIPP brines with no reducing agent present (both with and without carbonate), 0.1mM concentrations of Pu(VI) (approximately 24 mg/L) remained stable with respect to reduction for more than two years at 30°C.*

X.1.10.2 Response

This paragraph identifies a misrepresentation of the Choppin (1983 [DIRS 168395]) work on p. V-5. Text deleted on p. V-5 as part of this ERD.

X.1.11.1 Solubility Studies of $PuO_2(OH)·H_2O$ paragraph 3

> *Due to dominant Pu(VI)-sulfate complexation below about pH 4.5 the Theoretical* fO_2 *model predicts Pu concentrations to be nearly an order higher than if little or no sulfate were included (it is an artifact of the model input because the model charge balances on* $SO4^{2-}$*). Because of this chemical disparity between model input and experimental water chemistries, the dramatic rise in Pu solubility predicted by the model is probably not a realistic representation of dissolved Pu concentrations in low sulfate acidic solutions.(Figure 5 of*

Additional Information CR 12336.pdf shows the relative importance of PuO_2^{2+} *and* $PuO_2SO_4(aq)$*)*

X.1.11.2 Response

See Section X.1.7.2 for a discussion of [SO_4^{2-}].

The in-package pH never goes outside the range of 4.45 to 10.98 (SNL 2007 [DIRS 180506] and the corrosion product domain pH values never go outside the range of 6.25 to 9.16 (DTN: SN0703PAEBSRTA.002 [DIRS 186332]), so agreement of the model below pH 4.45 is not important and the use of a more conservative model outside this range is acceptable.

X.1.12.1 COMPARISON AGAINST EXPERIMENTAL COMMERCIAL SNF CORROSION STUDIES

The Adjusted Eh model is validated by comparing dissolved Pu concentrations predicted by the model against Pu concentrations measured in experiments reporting Pu concentrations released from dissolving CSNF. Data of Wilson (1990 [DIRS 100949 and 100793]) shown in Figure 7-1 of SNL (2007 [DIRS 177418]) include several data (10) that correspond to their 85°C experiments (series 3). Although three of those overlap data from Wilson's 25°C experiments, seven plot between one and four orders of magnitude below the 25°C data. By including them in Figure 7-1, the model looks a bit more conservative than if those data had been omitted. In addition, the majority of concentration data plotted in Fig. 7-1 (SNL 2007 [DIRS 177418]) are from the so-called "drip tests" on CSNF conducted at Argonne National Laboratory (CRWMS M&O 2000 [DIRS 131861 and 153105]). The Argonne tests were all conducted at 90°C. Judging from the Wilson data (Wilson (1990 [DIRS 100949 and 100793]), the data from the Argonne tests may be up to four orders of magnitude too low relative to 25°C (the temperature assumed for the model calculations). In addition, CRWMS M&O (2000 [DIRS 131861 and 153105]) reports concentration data for Pu-239 only (Tables 4-7), which constitutes approximately 60% of total Pu in those samples. Therefore, a more accurate representation of the ANL "drip-test" data is to apply two corrections: One is to correct the underestimate of total Pu associated with reporting only isotope 239 (dividing each value for [Pu-239] by 0.6. Note that this correction was already applied to the Wilson test data (Wilson (1990 [DIRS 100949 and 100793]) before plotting Figure 7-1 of [DIRS 177418]). A second adjustment for temperature is also required, and multiplying each [Pu] value (as corrected for isotope 239) by a factor of ten is approximately consistent with Wilson's 85°C test results (on average), as well as being consistent with the temperature dependence for Pu solubility reported by Efurd et al. (1998 [DIRS 108015]). That is, in order to estimate total [Pu] for the Argonne "drip tests" extrapolated to 25°C, the following correction was applied to each reported value for [^{239}Pu]*:*

$$[Pu]_{total} = 10 \times [^{239}Pu]/0.6$$

The corrected ANL data are shown in Figure 6 (Figure 4.2-1 in Additional information CR12336.pdf), which indicates that the "Theoretical fO_2*" model for Pu solubility more successfully bounds dissolved Pu concentrations from CSNF corrosion studies, whereas the "Adjusted Eh" model clearly does not. It is notable that the "Theoretical* fO_2*" model that* *assumes the lower fCO_2 (0.001%) actually follows the data rather well between about pH 5.5 and 7.5. In fact, the ANL "drip tests" may well have been depleted in CO_2 relative to ambient atmosphere because of the elevated temperature and the fact that vessels were only briefly opened to atmosphere during injections (CRWMS M&O, 2000 [DIRS 131861 and 153105]). The Wilson tests (Wilson 1990, [DIRS 100949 and 100793]) were conducted in sealed vessels under water, although 50 mL of air was bubbled through their solutions before each sampling. But both CO_2 and O_2 might be expected to drop below atmospheric levels during tests runs between samplings in those tests. Indeed, the Wilson data plot quite close to the trend of the data reported for $PuO_2(OH)_2{\cdot}H_2O$ in carbonate-free Ar (Kim et al. 1984 [DIRS 123597]); cf., Figure 4 (of Additional information CR12336.pdf).*

X.1.12.2 Response

The correction for total plutonium versus ^{239}Pu has been applied to the data and replotted in Figures 6.5-6, 7-1, V-2, V-8, and V-9.

The effects of temperature on fuel degradation rate, carbonate concentration, Pu(IV) colloid stability, and crystallinity are difficult to separate. However as the initiator states, "both CO_2 and O_2 might be expected to drop below atmospheric levels during tests runs between samplings in those tests." If CO_2 is depleted, the effect of temperature on carbonate concentration is reduced, and higher crystallinity is the likely reason the Wilson experiments showed lower concentrations in the higher temperature tests. Crystallinity increases with temperature and age, and once aged (under a decreasing radiation field), the solid remains aged (see pp. 50 to 51 rewrite per this ERD). Therefore the initiators suggestions that the 90°C Argonne tests *may be up to four orders of magnitude too low relative to 25°C,* and that the Argonne data should be multiplied *by a factor of ten,* as was done by the initiator in Figure 4.2-1, are not adequately supported.

Concerning the initiator's Figure 4.2-1, it is clear that when temperature, oxygen, and carbonate are varied, the model prediction can plot above or below the experimental data. The fact that the theoretical model with an fCO_2 of 10^{-5}, plots close to the "temperature-corrected" Argonne data proves nothing. Similarly, the comparison of the Wilson commercial SNF data (Wilson 1990 [DIRS 100949]; [DIRS 100793] with the Kim ([DIRS 123597]) Pu(VI), CO_2-free data, proves nothing, as two variables, O_2 and CO_2 are clearly different in these experiments. The plotting of Argonne National L drip test data uncorrected for temperature is appropriate in Figure 7-1 as discussed in Section X.1.6.i.2.

There will be an Eh gradient within the waste packages as long as commercial SNF and steel are present, as shown in Figure IV-2. A similar fCO_2 gradient may be envisioned. As plutonium diffuses or advects within these gradients, there will be an "effective Eh" and "effective fCO_2" that controls the plutonium concentration that exits the package. These effective controls change with time as the fuel and steel degrade and the opening to the air is widened. The Argonne drip tests and Wilson (1990 [DIRS 100949]) static tests shown in Figure 7-1 provide data on the plutonium concentrations that result from these effective controls. The adjusted Eh model plutonium concentrations and its uncertainty, lie higher than the mean and uncertainty of this empirical data leading to confidence that the adjusted Eh model provides a defensible upper bound for plutonium concentrations. Many other models may be envisioned that are more or less bounding or defensible. Professional judgment is used to pick the balance between bounding versus realistic models.

X.2 CR 13677 "INCORRECT PU LITERATURE DATA ILLUSTRATED ON FIGURE AND DTN"

Condition Description:

> *Figure V-8 of ANL-WIS-MD-000010 REV 06 from DTN: MO0707DISENSSI.000, file: "pu solf 104-3.jnb" has one set of data plotted incorrectly. Specifically, the solubility data from Rai et al. 2001 [DIRS 168392]) (0.4 mol/L NaClO4) are plotted versus observed pH instead of pcH. The actual values should all be shifted by 0.3 pH units higher. All other data appear appropriately plotted. The data are experimental data from literature and represents an inadvertent plotting error. This error does not impact the conclusions drawn from the figure or the AMR.*
>
> *The LA was searched and neither this figure nor the specific incorrect data appear in the LA. There is no anticipated impact to any ITS or ITWI SSCs, PCSA, TSPA or the FEIS/SEIS.*

Response:

Reexamination of "*pu solf 104-3.jnb*" from Output DTN: MO0707DISENSSI.000 (REV02) shows that the data from Rai et al. (2001 [DIRS 168392]) (0.4 mol/L $NaClO_4$) are plotted versus observed pH instead of pcH. Correcting this error changes Figure V-8 slightly as shown below but does not alter the conclusions. Spreadsheet "*pu solf 104-3.jnb*" was deleted from the DTN. The contents of this file that was used in the report was transferred to "*pu solb 104-3.xls*". All errors within "*pu solb 104-3.jnb*" associated with CR 13677 have been updated in "*pu solb 104-3.xls*" used to create Figure V-8. This update is presented in Rev 03 of DTN: MO0707DISENSSI.000.

X.3 CR 14113 "PU LOG K UNCERTAINTY NOT UPDATED IN FIGURES"

Condition Description:

> *When the log K uncertainty was changed from 1 sigma = 1.0 to 1 sigma = 0.7, several graphs in ANL-WIS-MD-000010 Rev 06 should have also changed but still retain the old uncertainty value. These figure need to be updated as well as 2 output DTNs from the model report.*
>
> *Figures needing adjustment include:*
>
> ***Figure 6.5.6**, Comparison of Experimental Data with the Predictions of the Plutonium-Solubility Model*
> ***Figure 7-1**, Comparison of Experimental Data with the Predictions of Plutonium-Solubility Model at log* $fCO_2 = -3.5$
> ***Figure V-2**, Comparison of the Theoretical (Atmospheric)* fCO_2*,* PuO_2*(hyd,aged) Model with Pu Solubility Measurements.*
> ***Figure V-8**, Pu Solubility Given by the Eh Model*
> ***Figure V-9**, Comparison of Experimental Data with the Predictions of the Plutonium-Solubility Using Equation V-5.*

DTNs and associated spreadsheets affected include:

MO0707DISVALID.000. Dissolved Concentration Limits Files for Validated Models. Pu model-lab.xls
MO0707DISENSSI.000. Dissolved Concentration Limits Files for Sensitivities and Validation.

Wilson-ANL.xls
Simple Pu solb.jnb
Pu solb 104-3.jnb.

This error does not impact the conclusions drawn from these figures or the AMR. The condition affects only figures in the AMR that are used solely for demonstrative purposes. It does not affect TSPA since the TSPA uses the updated values presented in the AMR.

Changes to these figures will affect LASAR Figures 2.3.7-35, 2.3.7-37, and 2.3.7-38, but does not affect any conclusions drawn from these figures.

Response:

Re-examination of "*Pu model-lab.xls*" (DTN: MO0707DISVALID.000), "*Wilson-ANL.xls*", "*simple pu solb.jnb*", and "*pu solb 104-3.jnb*" (DTN: MO0707DISENSSI.000) shows that a 1σ = 1.0 was used in the spreadsheets instead of a 1σ = 0.7 for the Log K uncertainty on plutonium. Correcting this error changes Figures 6.5-6, 7-1, V-2, V-8, and V-9 slightly but does not alter the conclusions. Spreadsheets "*simple pu solb.jnb*" and "*pu solb 104-3.jnb*" were deleted from DTN: MO0707DISENSSI.000. The contents of these files that were used in the report were transferred to "*pu solb 104-3.xls*". Errors within "*simple pu solb.jnb*" and "*pu solb 104-3.jnb*" associated with CR 14113 have been updated in "*pu solb 104-3.xls*". Updated versions of "*pu solb 104-3.xls*" and "*Wilson-ANL.xls*" are presented in Rev 03 of DTN: MO0707DISENSSI.000. Updated version of "*Pu model-lab.xls*" is presented in Rev 01 of DTN: MO0707DISVALID.000. There is no impact to TSPA because the correct σ was implemented in TSPA.