HLWYM HEmails

From: Murphy, William [WMurphy@csuchico.edu]
Sent: Wednesday, February 09, 2005 3:42 PM
To: David Pickett
Subject: RE: Np solubility
Attachments: Distributions.MRS04.pdf; ConLim9.15.doc

Follow Up Flag: Follow up
Flag Status: Flagged

David,

Some of my recent comments on Np are in the attached documents; more by phone, etc.

Bill

-----Original Message-----
From: David Pickett [mailto:dpickett@cnwra.swri.edu]
Sent: Wednesday, February 09, 2005 9:51 AM
To: Murphy, William
Subject: Np solubility

Bill,

I'm muddling through neptunium solubility limit (or maybe "concentration limit."). Was DOE's secondary phase Np "concentrating factor" model completely discredited? I'm familiar with uncertainty surrounding the lab data, but what about the approach to predicting [Np]? It fit well with the Wilson leach data.

Dick Codell wants the Np solubility limit abstraction in TPA to better fit the leach test data. I'm pointing out that you shouldn't expect a true solubility limit to do that, but he also wants to consider secondary phase control, rather than pure Np phase control.

I don't think I've yet seen what you may have written on the topic for Bobby in the last couple of years. I do have something you wrote in December 1999.

David

Hearing Identifier: HLW_YuccaMountain_Hold_EX
Email Number: 773

Mail Envelope Properties (15E29EFEC45DC34F8A91C46CBE80BF440A45F061)

Subject: RE: Np solubility
Sent Date: 2/9/2005 3:42:20 PM
Received Date: 2/9/2005 3:43:08 PM
From: Murphy, William

Created By: WMurphy@csuchico.edu

Recipients:
"David Pickett" <dpickett@cnwra.swri.edu>
Tracking Status: None

Post Office: ESCHE.csuchico.edu

Files	Size	Date & Time
MESSAGE	1044	2/9/2005 3:43:08 PM
Distributions.MRS04.pdf	89245	
ConLim9.15.doc	69696	

Options
Priority: Standard
Return Notification: No
Reply Requested: No
Sensitivity: Normal
Expiration Date:
Recipients Received: Follow up

FIGURE WITHHELD UNDER
10 CFR 2.1005(h)

FIGURE WITHHELD UNDER
10 CFR 2.1005(h)

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10 CFR 2.1005(h)

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10 CFR 2.1005(h)

Commentary on the Technical Basis for Parameter Values and Probability Distributions for Radionuclide Concentration Limits for NRC/CNWRA Yucca Mountain Performance Assessment Source Term Modeling

William M. Murphy

Prepared for CNWRA
September 15, 2003

I. Scope and Executive Summary

This report addresses concentration limits for performance assessment (PA). The source term for each radioactive element in PA models is limited by its release rate or by its concentration limit. General controls on concentration limits are discussed initially particularly as they are applicable to PA. The distinction between natural or modeled concentrations and concentration limits is important and sometimes confused in PA analyses. Specific conditions at Yucca Mountain are evaluated to provide a context for evaluating and selecting concentration limits. Given the long anticipated time of waste containment at Yucca Mountain and the strong geochemical buffering capacity of the natural environment, natural conditions should be emphasized in evaluating eventual concentration limits for radioactive elements.

Concentration limits are subject to large uncertainties and conditions controlling concentration limits are subject to large variations. Uncertainties and variations are reasonably addressed in probabilistic PA using distributions from which values are sampled. The technical basis for distributions of radioactive element concentration limits is presently very weak. For many radioactive elements the NRC/CNWRA PA doesn't consider distributions, only fixed values. Log normal distributions are sometimes advocated, but their justification is weak, and they are not conservative because they emphasize low concentration limits within a range of values. Additional work in this area is warranted.

The present approach to concentration limits by DOE is given in Revision 2 of the AMR on Dissolved Concentration Limits of Radioactive Elements. This report may not be released formally, but the version dated June 2003 (OCRWM, 2003) is reviewed at some length in this report. This preliminary information should be used with sensitivity until the report is formally issued by DOE. The DOE approach is based on thermodynamic modeling and generation of functional relations between concentration limits and principal intensive variables, pH and CO_2 pressure. Variability parameters are also used to qualify the concentration limits. This approach is complicated and challenging to review or to revise. However, it provides a valuable independent approach to compare to results from usual concentration limit evaluations.

Ranges of concentration limits for key radioactive elements are compared from the NRC/CNWRA approach in TPA 4.0, the SKi Project-90 evaluation, and the latest DOE AMR. In general there is a good correspondence. Detailed differences provide

indications of areas where additional work would be valuable to justify the concentration limits used for the NRC/CNWRA PA.

A discussion is provided of solubility limits for individual radioactive elements identifying possible problems or areas for future work. Finally a summary of recommendations is given.

This report does not provide a definitive or final recommendation for radioactive element concentration limits for NRC/CNWRA PA. A variety of unresolved issues are defined in this report that should be addressed before parameter values and distributions are confirmed.

II. Controls on Concentration Limits

Concentration limits for PA are sometimes characterized as maximum concentration limits or as dissolved concentration limits and are commonly called solubility limits or solubilities. In this report the term solubility denotes a concentration controlled by thermodynamic equilibrium as expressed in the law of mass action. Thermodynamic solubility constraints are commonly used in PA source term studies to set maximum concentration limits.

Radioactive element concentration limits provide a mechanism for isolation of wastes and contribute positively to repository performance. Low concentration limits are good for waste isolation. Upper limits to concentration limits are conservative for PA. Recently Mohanty et al. (2003) illustrated through sensitivity studies that concentration limits are a major barrier in Yucca Mountain PA.

Likely concentrations or model concentrations in PA do not generally correspond to maximum concentration limits. Conditions for which PA model concentrations correspond to PA concentration limits occur at high release rates (relative to transport rates away from the source by diffusion or advection) and at locations near the source. For slow release rates and for elements that do not precipitate as solid phases under repository conditions, concentration limits are never achieved in PA models. Modeled or expected radioactive element concentrations commonly diminish with distance from the source because of transient sorption or matrix diffusion effects. Concentrations also diminish with radioactive decay, although certain radionuclide inventories increase with time due to ingrowth.

Concentration limits, their uncertainties, and their distributions must be evaluated in the context of natural aqueous concentrations. Elemental concentrations in geochemical systems range over many orders of magnitude and may be controlled or influenced by numerous coupled processes summarized in the following list.

1. Release rates from source materials

2. Solubility limiting phases containing the element as a primary component, which is sometimes called pure phase solubility

3. Equilibrium between the component in the aqueous phase a minor component of a solid (e.g., ion exchange, solid solution, coprecipitation)

4. Chemical kinetic balances between sources and sinks, which may approach or achieve steady states

5. Sorption or matrix diffusion, which, however, do not affect concentrations under steady state conditions

6. Solvent properties controlling aqueous speciation, such as effects of temperature, pH, oxidation-reduction potential (Eh), and concentrations of complexing aqueous species such as bicarbonate, chloride, sulfate, and fluoride

7. Colloid formation and stability

This report focuses on maximum concentration limits for the PA source term, which may depend on all of these processes. Primary areas of focus in concentration limit studies are solubility limiting phases (2,3) and solvent properties (6). Kinetic controls on concentration limits (4) are commonly invoked to explain experimental or natural data, but their quantitative applications in PA are limited because of large uncertainties. Release rates from source materials (1) potentially affect concentration limits in a secondary manner by producing states of supersaturation. Sorption or matrix diffusion (5) could affect source concentrations on a transient and limited basis, and are treated separately in PA consideration of radionuclide transport. Similarly, colloids (7) are treated separately in PA.

Thermodynamic equilibrium provides an attractive approach to constrain concentration limits. An aqueous solution at equilibrium with a solid phase is saturated with respect to that solid. Thermodynamic activity products for the dissolution reaction that are higher than the equilibrium condition represented by the equilibrium constant correspond to supersaturated solutions. Supersaturated solutions are thermodynamically unstable or metastable. Dissolution reaction activity products that are lower than the equilibrium constant correspond to undersaturated solutions. In a closed, isothermal, one component system, thermodynamics precludes solid dissolution to produce concentrations in excess of the equilibrium concentration for that solid, i.e., a supersaturated solution. In this sense, thermodynamic solubility provides maximum concentration limits that are firmly based on theory. In practice, however, geochemical solutions commonly achieve conditions of supersaturation by a variety of processes, notably irreversible dissolution of an unstable phase to produce solutions that are supersaturated with respect to a more stable solid phase. Variations in temperature or other intensive properties of the system can also lead to supersaturated conditions.

Transient conditions can lead to supersaturation by dissolution under one set of conditions followed by evolution to conditions for which the equilibrium solubility is lower. Mixing different solutions can also generate supersaturated solutions. Metastable supersaturation is sustained by slow nucleation and growth rates of solid phases, particularly at low temperature. Hence, equilibrium solubilities do not always provide conservative maximum concentration limits.

III. Controls on Concentration Limits at Yucca Mountain

Radionuclide releases, for which source term concentrations are applicable, will occur after a long period of time under conditions at Yucca Mountain that can be reasonably anticipated. The thermal period will be over and geochemical conditions will have returned to those corresponding to natural conditions with additional effects of introduced materials and residual effects of the thermal period. Aqueous geochemical conditions will be dominated by the natural system, which will closely resemble conditions prior to the repository (e.g., Browning et al., 2000). Concentrations limits for PA need not consider temperatures other than 25°C and must focus on oxidizing, dilute aqueous solutions.

Near field material reactions and thermal perturbations including dissolution and precipitation of mineral phases, oxidation of EBS materials, and variations in porosity and permeability will have long term effects. Solid phases in the near field will be strongly affected by alteration products of EBS materials. Concentrations may be controlled by reactions between these secondary products of waste form or engineered barrier system (EBS) alteration and solutions with chemistries dominated by natural conditions. However, these concentrations are unlikely to be applicable as concentration limits for PA. The important difference between concentrations controlled by release from secondary products and concentration limits distinguishes the source term approach developed by Murphy and others (Murphy and Pearcy, 1992; Murphy and Codell, 1999) from that developed by Chen and others (e.g., Chen et al., 2002). Both approaches rely on the realistically important role of coprecipitation of radionuclides in uranyl secondary phases to control the source term. However, the modeling approach taken by Murphy and others uses this mechanism as a control on release rates and concentrations, whereas the approach by Chen and others mistakenly confounds these model concentrations, and the experimental values on which they are based, with concentration limits.

Oxidation reactions at Yucca Mountain will exert a primary control on containment and on the source term. Primary release rates for many radionuclides will be controlled by oxidation rates of waste forms. The oxidation state of species has large effects on aqueous solubilities and concentration limits. Yucca Mountain is highly oxidizing above the water table, is buffered by atmospheric oxygen, and contains minimal natural reducing capacity in solid, aqueous, or gas phases. In contrast, metallic EBS components (e.g., alloy C-22, stainless steel, zircalloy, and titanium) are reducing, creating oxidation-reduction potentials lower than the stability limit of water at atmospheric pressure. Uranium in spent nuclear fuel is quadravalent, which is unstable relative to oxidized, hexavalent uranium at atmospheric oxygen pressures. Reduced

components of the near field will be slowly armored by oxidation products, which will influence near field transport.

For purposes of PA source term concentration limits, it is reasonable to focus on oxidizing conditions for several reasons. Oxidizing conditions will ultimately prevail at Yucca Mountain because of the unlimited oxidation capacity provided by atmospheric oxygen. The releases at the source will occur after long times when gas and aqueous geochemical conditions will have returned to conditions controlling primarily by natural processes. Releases of most radionuclides from the predominant waste form, spent nuclear fuel, will occur as it is oxidized. Solubilities of redox sensitive elements of concern are greater under oxidizing conditions than under reducing conditions, so solubilities under oxidizing conditions provide conservative upper limits to concentrations.

Relatively reducing conditions will develop on transient local and temporal scales because of EBS alteration. Relatively reduced solutions will potentially migrate along pathways of water flow and radionuclide transport. Radionuclide species that are initially reduced but potentially oxidized may be stable along these paths. Some reduced species may remain thermodynamically metastable under oxidizing conditions. For purposes of setting upper concentration limits, reduced species should be considered if solubilities of the reduced species exceed those of the oxidized form, particularly if reduced forms are indefinitely metastable under oxidizing conditions.

IV. Variation and Uncertainty in Concentration Limits

Concentration limits are subject to large variability and large uncertainty. Concentration limits depend on variable conditions including temperature, pH, oxidation potential, and solid phase assemblage. Uncertainties arise from indeterminate controls on concentration limits, e.g., the identity and properties of aqueous species and solubility controlling solids, and metastability.

Probabilistic PA methods commonly sample concentrations limits from distributions intended to represent variability and uncertainty for each radioactive element. Alternatively, probabilistic PA may sample distributions of environmental conditions and then calculate corresponding concentration limits based on empirical or theoretical relations between environmental conditions and concentration limits. The practical basis for concentration limit ranges may include ranges of measured concentrations in experiments or in nature or ranges of calculated concentrations based on solubility or kinetic relations, ranges of conditions, and ranges of values for uncertain parameters such as equilibrium constants.

Distributions of maximum concentration limits are distinct from distributions of concentrations because the limiting values represent only a portion of the range of concentrations. This distinction is stressed in this report. For example, natural concentrations or natural concentration distributions do not generally correspond to solubilities or concentration limit distributions that are applicable to PA source term

constraints. For PA and in nature, distributions of concentrations limits do not correspond to distributions of concentrations.

Characterizations of populations of concentration limits used in PA include normal, uniform, log normal, log triangular, constant, and other distributions. Although limits on concentration limits are commonly based on empirical data and geochemical modeling, distributions used in PA commonly have a weak empirical or theoretical basis. The present DOE evaluation for concentration limits (OCRWM, 2003) makes the following argument: "The solubility data provided in this report are given as log solubility values. The uncertainties in them are expressed as normal distributions of the log solubility values because they are derived from uncertainties in the standard thermodynamic properties, which are given as normal distributions." This rationale is partially applicable to concentration limits. Logarithms of maximum equilibrium concentrations (solubilities) are related by the law of mass action for dissolution reactions to sums of standard Gibbs free energies. Uncertainties in standard state thermodynamic properties may or may not be represented by populations that are normally distributed. However, equilibrium concentrations (solubilities) also depend primarily on multicomponent solution compositions, which are controlled by a suite of geochemical processes and properties, not just standard state free energies.

Distributions of geochemical data are frequently described according to log normal distributions. A basis was proposed for log normal distributions of geochemical concentrations in the 1950s (e.g., Ahrens, 1954a,b). Concentrations are bounded by zero at the low end, and distributions of geochemical concentrations commonly exhibit a tail of high values. These characteristics tend to make log transformations of populations appear to be normal (i.e., log normal). However, strict examinations of geochemical concentration populations show significant deviations from log normal distributions (e.g., Link and Koch, 1975; Reimann and Filzmoser, 2000). Also, the common absence of analytical values below detection limits complicates interpretations of natural concentration distributions (e.g., Helsel, 1990). In general, geochemical distributions result from differentiation processes and mixing processes, which tend to operate in opposition to each other, but which often combine to produce a given population. Combinations of differentiation and mixing processes can lead to a variety of distributions. Allègre et al. (1995) proposed that geochemical mixing processes lead to normal distributions and that differentiation leads to fractal or multifractal distributions, which may be log normal. A study of the empirical and theoretical basis for concentration limit distributions for PA applications has been initiated in the present work, but remains incomplete.

Uncertainties in concentration distributions are important for PA, and have not been adequately evaluated. A distributional sensitivity analysis showed that dose responses are significantly affected by improper choice of distribution functions (CNWRA, 2002b). Concentration limits were not among the variables tested in this analysis. Given upper and lower bounds on concentration limits, a log normal or log uniform distribution will result in many more low values in the population than a normal or uniform distribution with the same bounds. In the absence of a theoretical or empirical

basis, log distributions of concentration limits are not conservative for PA compared to linear distributions. (Ironically, the other primary geochemical parameter in PA, the solid-liquid distribution coefficient or Kd, exhibits the reverse effect; small Kds are conservative.)

V. General Comments on the Current DOE Approach to Concentration Limits

The current basis for concentration limits for the DOE License Application PA is described in the AMR on Dissolved Concentration Limits of Radioactive Elements (OCRWM, 2003). The general DOE approach to constrain concentration limits is to postulate a range of water compositions and to calculate (model) solubilities for radioactive elements at equilibrium with these waters. Water chemistries were based on J-13 well water with large variations in pH and CO_2 partial pressure. These variations required corresponding changes in water chemistry to maintain thermodynamic correctness. For example, sulfuric acid and sodium hydroxide were added to generate acid and base solutions, respectively, invoking sources of sulfur from metal and glass alteration, respectively. Solubility calculations were performed for 25°C and oxidizing conditions.

Model solubilities were based on thermodynamic properties for solids and aqueous species and extended Debye-Hukel activity coefficient (b-dot) relations given in the EQ3NR database (data0.ymp.R2). This database depends strongly on recent NEA compilations of thermodynamic properties for actinides. The NEA compilations tend to impose scientific conservatism by omitting species for which data are uncertain. However, omitting species is not conservative for PA applications because it can lead to calculated total concentrations that are smaller than if the omitted species were included. A continuous evaluation of the properties of relevant aqueous and solid species is recommended because of this difference in objectives and approach.

Extremely broad ranges of pH and CO_2 pressure were considered in the DOE solubility studies. The range in pH (3 to 11) was intended to cover the range of in-package conditions for codisposal materials. The range of CO_2 pressure (10^{-5} to $10^{-1.5}$ bar) was selected with little apparent basis, although it encompasses any reasonably expected values. In many cases these broad conditions, coupled with the sulfuric acid and sodium hydroxide treatments to achieve desired pH, led to aqueous solutions or solid-solution equilibria that are thermodynamically untenable. Attempts to achieve thermodynamic (EQ3NR) models for these systems failed. A common feature of the concentration limits tabulated in OCRWM (2003) is arbitrarily high values adopted for conditions and systems that failed to permit a valid thermodynamic model to be computed.

In addition to ranges of calculated solubilities for variable solution compositions and solid phases, "variability terms" were included for some radioactive elements to accommodate uncertainties in thermodynamic data or in potential aqueous complexation effects of fluoride. The treatment of fluoride variations is conservative, particularly in absence of likely mechanisms for generating solutions of high fluoride concentration.

The DOE approach to concentration limits is based on postulated ranges of conditions and thermodynamic modeling. Functional relations are developed between calculated solubilities and the intensive parameters, temperature, pH, and log CO_2 pressure. Then additional uncertainty functions are supplemented. Concentrations limits used in DOE probabilistic PA will be derivative properties. Parameter sampling may occur for pH, temperature, and CO_2 pressure. Then, based on the functional relations derived from thermodynamic modeling, values of solubilities will be calculated. This approach has a reasonable basis and provides a valuable alternate evaluation of distributions of solubility limits. It deviates from the established approach of characterizing concentration limit distributions and sampling from those distributions. This derivative approach of DOE is based on suites of thermodynamic models and abstraction of their results in functional relations specific to the Yucca Mountain PA problem. It is challenging to make comparisons between the DOE derivative approach and one that uses sampling from a distribution of concentration limits. This approach complicates any changes based on new data. For example, low temperature properties of solubility controlling solid phases are critical in the thermodynamic modeling approach of DOE, and they are highly uncertain. The likely acquisition of new data for these phases would be very difficult to incorporate in the existing DOE concentration limit approach because it would require many new thermodynamic (EQ3NR) models to be generated and their results to be abstracted. Nevertheless, it would be useful to determine the concentration limit distributions that result from this derivative approach and used in the DOE PA, and to compare these distributions with others.

VI. Comparisons of Concentration Limits in Three Compilations

A first order evaluation of CNWRA/NRC concentration limits is provided by comparison to values determined in different studies. A summary is provided in Table 1 of concentration limits from the CNWRA/NRC TPA 4.0 (CNWRA, 2002a), the SKi Project-90 (Andersson, 1988), and the DOE concentration limits AMR rev. 02 (OCRWM, 2003), which are largely independent. The SKi compilation is for oxidizing conditions in generic crystalline rocks. SKi reported estimated values as well as upper and lower limits, and these are also reported in Table 1. DOE values were extracted from tables of solubilities provided as functions of pH and log CO_2 pressure. As discussed in section V, the ranges of these parameters considered by DOE are very broad. For the comparison presented in Table 1, maximum and minimum solubility values were selected from the DOE tables for reasonably realistic conditions of pH between 7 and 9 and of log CO_2 pressure (bars) between –2.5 and –3.5. In some cases, DOE models failed to achieve calculated solubilities for all conditions even within these ranges. DOE concentration ranges reported in Table 1 only reflect solubilities that were calculated. Also, stochastic variations applied by DOE to accommodate uncertainties in solid phase identities or properties or fluoride complexation are not included in the values represented in Table 1. No values were reported for DOE for several elements that were screened out of their analyses because of small predicted effects on performance.

Table 1. Concentration Limits for Radioactive Elements (log_{10} kg/m^3)

Element	Source	Minimum	Estimated/ Fixed Value	Maximum
Am	NRC	-7.62		-3.62
	SKi	-8.31	-4.01	-0.61
	DOE	-5.12		-2.96
C	NRC		1.15 (high[1])	
	SKi		high	
	DOE		high	
Cl	NRC		1.56 (high)	
	SKi		high	
Cm	NRC		-3.62	
	SKi	-8.31	-4.01	-0.61
Cs	NRC		2.13 (high)	
	SKi		high	
	DOE		high	
I	NRC		2.11 (high)	
	SKi		high	
	DOE		high	
Nb	NRC		-6.03	
	SKi	-7.03	-6.03	-5.03
Ni	NRC		-0.96	
	SKi	-4.23	-1.23	-0.77
Np	NRC	-2.92	-1.47[2]	-0.62
	SKi	-5.63	-0.45	-0.45
	DOE	-3.75		-0.97
Pb	NRC		-4.18	
	SKi	-5.68	-3.68	-1.68
	DOE	-6.00		-4.00
Pu	NRC	-5.62		-3.62
	SKi	-9.14.	-6.01	-4.83
	DOE	-4.75		-3.69
Ra	NRC		-4.64	
	SKi	-5.65	-4.04	-1.65
	DOE		-4.70, -2.92[3]	
Se	NRC		1.90 (high)	
	SKi	-0.10	0.90	1.60
Tc	NRC		2.00 (high)	
	SKi		high	
	DOE		high	
Th	NRC		-3.64	
	SKi	-7.22	-6.40	-5.29
	DOE	-5.40		-2.37
U	NRC		-2.12	
	SKi	-4.45	-0.45	-0.45
	DOE	-2.79		-0.73

Footnotes for Table 1.

1. High applies to elements that were deemed not to be controlled by concentration limits because of their high solubilities. For NRC/CNWRA entries, default "high" values are reported in Table 1 corresponding to concentrations of 1 molar.
2. Neptunium concentration limits are represented as a log triangular distribution by CNWRA/NRC. The midpoint of the distribution is reported in the Estimated/Fixed Value column of the Table.
3. DOE uses two fixed values for radium solubility applicable to conditions above (higher solubility) and below (lower solubility) pH 7.75.

VII. Comments on Concentration Limits for Selected Elements

1. High solubility elements: C, Cl, Cs, I, Se Tc. In compilations by NRC/CNWRA, SKi, and DOE (Table 1) these elements, with the following exceptions, were assigned high or unlimited solubilities indicating that release rates, not solubility, will control the source term. Cl and Se were not considered by DOE. Se was assigned concentration limits by SKi, which are slightly lower than the default high solubility (1 molar) assigned by NRC/CNWRA. These results suggest that if Se release contributes significantly to doses, then a more detailed analysis may reduce conservatism and permit application of concentration limits.

In the sensitivity study by Mohanty et al. (2003) the high solubility elements noted in this section were correctly controlled by their release rate in the bathtub model. However, in the flow-through model, Tc-99, Cs-135, and I-129 all were solubility limited for a portion of the time. This result indicates that the default 1 molar "high" solubility limit used for NRC/CNWRA PA is not sufficiently high to assure that all radioactive elements without established solubility limits are limited by release rates in the PA models.

2. Neptunium. Np is important to PA because its solubility may be high, its inventory fairly high and increases due to ingrowth, it is poorly sorbing, and its half life results in significant activity at times when doses may occur. Np solubility is complicated because it exists in multiple oxidation states, it forms stable carbonate complexes, and it occurs in a variety of solid phases having vastly different properties.

NRC, SKi, and DOE have closely comparable ranges for Np solubility (Table 1). The log triangular distribution adopted by NRC is an approximation of the beta distribution recommended for TSPA-95.

Extensive efforts by DOE to develop models to constrain Np solubility by coprecipitation make useful recognition of the role of secondary uranyl phases. However, solid solution relations are difficult to invoke as a solubility limit as advocated by Chen et al., (2002). In contrast, solid solution (coprecipitation) relations may be used to constrain release rates rather than concentration limits (Murphy and Codell, 1999).

Comparison of Np concentrations in spent fuel experiments to hypothetical solubility calculations is comparing different things. Nevertheless, the DOE AMR states "This comparison shows that the Np_2O_5 solubility model developed in this report is conservative and thus is adequate for TSPA use." This conclusion is dubious. Concentrations from experiments that are not designed as solubility studies generally do not provide limiting concentrations, so comparisons to these values is not validation of solubility limit estimations.

Recent work by Fortner et al. (2003) casts doubt on previously reported evidence of Np substitution in secondary uranyl phases. Although secondary uranyl phases may play a dominant role in controlling releases of Np and other radionuclides, the mechanisms and quantitative characterization of this process is poorly constrained at present. It is reasonable that DOE and NRC regard this mechanism as an alternate model at present.

3. Plutonium. The DOE Pu solubility model is very complicated. The Pu solubility covers the range spanned by PuO_2(c) and PuO_2(hyd, aged) models, neither of which is realistic, but which are presumed to bracket a more realistic radiation damaged less crystalline PuO_2. DOE states in the AMR "It is appropriate in determining the mean of solubilities for this abstraction to average the free energies, or logs of the solubilities. Therefore, the mean of the logarithm of the recommended plutonium solubility was set equal to the average of log[Pu]1 and log[Pu]2. The uncertainty associated with this solubility is represented by a stochastic variable, e1. Since the two end member solids (PuO_2 and PuO_2(hyd,aged)) would be converted to PuO_2(lc) rapidly, low probabilities should be assigned to them. Thus, e1 is assigned a triangular distribution with its peak (b) equal to 0 and its two vertices equal to the distances between the mean value of log[Pu] and $\log[Pu]_1$ and between that and $\log[Pu]_2$." This line of argument is fairly logical, but speculative, certainly not a validated model for Pu solubility. The lower limit (least conservative limit) of the Pu distribution is based on the maximum difference between the crystalline and hydrated PuO_2 solubilities for all pH and CO_2 conditions, which is lower than justified by the data for pH and CO_2 conditions in general.

Pu solubility limits used by CNWRA/NRC correspond closely at the upper end to those determined by the DOE interpretation for a reasonable range of pH and CO_2 pressure. The lower end of the CNWRA/NRC range is somewhat lower than the lower end of the DOE range. However, the ranges reported for DOE in Table 1 do not include the e1 triangular stochastic variation, which is large (3.3 orders of magnitude).

4. Lead. Solubility limits for Pb used by CNWRA/NRC and DOE are closely comparable. SKi values range to much higher (more conservative) values. DOE treatment of Pb solubilities is based on a false correspondence between natural concentrations and concentration limits. DOE states "Because the lead sinks in the waste package environment are similar to a number of those that control lead in the environment, it is reasonable to expect dissolved lead levels to roughly reflect natural distributions (i.e., levels between 1 and 100 ppb). This corresponds to a range of 4.8E-9 to 4.8E-7 M. It is therefore recommended that TSPA use a log-uniform distribution, with a minimum of

4.8E-09 and a maximum of 4.8E-7, to constrain lead solubility." However, natural Pb concentrations are not solubilities. Solubilities for PA must be upper limits to concentrations not expected concentrations. Also, as noted elsewhere, log distributions are not conservative for concentration limits, even if the ranges are well established. Given the inappropriate basis for the DOE concentration limits for Pb, and the considerably higher recommended limits for Pb in the SKi work, a reevaluation of Pb concentration limit for NRC/CNWRA is warranted. The abundance of natural Pb data should facilitate this study. However, natural data must be evaluated cautiously because of the distinction between concentrations and concentration limits emphasized in this report.

5. Americium, Curium, Niobium, Nickel, Radium, Thorium, Uranium. Am limits extracted from the new DOE evaluation (Table 1) are higher than values used by NRC/CNWRA, and SKi values extend to much higher values. A reevaluation of NRC/CNWRA Am solubility limits is warranted. Evaluations of solubility limits for Cm are constrained by sparse data. Realistically Cm will be incorporated in secondary phases and its release will be controlled by the kinetics of alteration of secondary phases or the solubilities of secondary phases, not by solubility of a Cm phase. NRC/CNWRA uses a fairly high (conservative) fixed value for Ni, which could probably be reduced by detailed analyses of natural and experimental data if warranted by effects of Ni in PA analyses. Ra concentration limits for NRC/CNWRA PA are generally lower than those proposed by DOE and SKi, suggesting that NRC/CNWRA values may not be conservative. $RaSO_4$ is the solubility limiting phase commonly selected for Yucca Mountain analyses. However, it seems likely that Ra would be incorporated as a trace constituent in carbonate minerals and would be release according to carbonate system chemistry. Fixed values for Th and U concentrations in NRC/CNWRA studies appear to be reasonable, but fail to capture uncertainty and variability in their concentration limits. Given the abundance of these elements in nature and the abundant U minerals associated with U deposits. U data could be useful to evaluate in detail the justification for concentration limit distributions as discussed in section IV.

VIII. Recommendations

Citations for NRC/CNWRA PA concentration limits (CNWRA 2002a) largely date to values used in DOE's TSPA-93 and Gautier (1993). With a few recommendations noted in section VII, these values appear mostly to be reasonable based on evaluations of newer data and based on comparisons to recent DOE compilations (section VI). However, Gautier (1993) was never published, and an updated comprehensive evaluation is warranted. This report is an initiation of such an evaluation, which is incomplete.

DOE concentration limits need close scrutiny for conservatism and validation. Several apparent problems have been noted in this report, e.g., for lead based on natural concentrations (not concentration limits) and for the alternate neptunium coprecipitation model, which is a release rate process, not a concentration limit process. However, the independent approach and data used to generate the current DOE concentration limits

(solubilities) (OCWRM, 2003) provides a very useful resource for comparison to other data sets and for evaluating distributions.

Correlations have been generally neglected among concentration limits for different radioactive elements used in PA. The thermodynamically based approach taken by DOE and the derivative method of selecting concentration limits by sampling pH and CO_2 pressure should provide a useful set of data to evaluate correlations between concentration limits.

The importance of distributional uncertainty has been emphasized recently in CNWRA (2002b) for parameters other than concentration limits. The empirical or theoretical basis for distributions of concentration limits is presently weak. Log normal distributions, which are commonly used, and partially rationalized using discredited interpretations of geochemical data, are not conservative for PA purposes. Developing a basis for concentration limit distributions is an area of investigation that should be pursued.

IX. References

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