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ATTN: Document Control Desk
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Subject: First Draft of Radionuclide Solubility in Cement-Based Material Pore Fluids [Intermediate Milestone (IM) 14003.01.007.200]

Dear Mr. Fuller:

This letter transmits the subject deliverable. In the fiscal year 2008 operations plan, this deliverable is identified as IM 14003.01.007.200 Draft Letter Report on Solubility of Radionuclides in Grout Pore Fluids. The title of the report has been changed as indicated to better reflect the contents.

This first draft report summarizes literature data and new geochemical models on radionuclide solubility limits in pore waters of cement-based materials. Consideration of solubility limits to dissolved concentrations is one component of understanding radionuclide release processes. This report is intended to assist staff in reviewing radionuclide release abstractions in the U.S. Department of Energy performance assessment models for cement-based disposal environments.

Please do not hesitate to contact me (210.522.2139) or Dr. David Pickett (210.522.5582) with any questions about the subject report.

Sincerely,

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RADIONUCLIDE SOLUBILITY IN CEMENT-BASED MATERIAL PORE FLUIDS

Prepared for

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Contract NRC–02–07–006

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QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: No original data was generated from the analyses presented in this report. Sources for data cited in this report should be consulted for determining the level of quality of those data.

ANALYSES AND CODES: This report includes results of calculations performed using Geochemist's Workbench® (RockWare, Inc., 2005). Data reduction and plotting were accomplished using Microsoft® Excel® (Microsoft Corporation, 2002). Calculations were documented in Scientific Notebook 877E.

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Microsoft Corporation. "Excel." Redland, Washington: Microsoft Corporation. 2002.

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1 RADIONUCLIDE SOLUBILITY LIMITS IN CEMENT-BASED MATERIAL PORE FLUIDS

1.1 Introduction

An important variable in groundwater pathway performance assessments is the contaminant concentration in water at the source. Models for contaminant release vary widely, but typically include a maximum bound on concentration based on a solubility limit. For example, isotopes of a radioelement may be modeled to be released congruently as a nuclear waste form dissolves in contact with water, but the radionuclide concentrations in that water can be capped at an elemental concentration that is controlled by the solubility of a solid phase of that element.

In cement-based disposal facilities at the Savannah River Site (SRS) and Idaho National Laboratory (INL), including both grouted tanks and monolithic waste forms, the U.S. Department of Energy (DOE) has typically modeled radionuclide release using a partition coefficient or K_d to constrain radionuclide concentration [Rosenberger, et al. (2005); DOE–ID (2003)]. This coefficient, which is also applied in many groundwater transport models, defines the radionuclide concentration by assuming a constant ratio between the mass on the solid waste form and the mass in solution. For the SRS and INL models, the K_d values are chosen to be appropriate for a cementitious environment (e.g., Bradbury and Sarott, 1995). This approach may not always be the most appropriate for a release calculation, particularly if the waste form is dissolving and the chemical environment is potentially dynamic. Furthermore, if a radionuclide is released at the margin of the cement-based waste form, a release model K_d that assumes sorption to cement-based material solids may not be appropriate.

It is important, then, to consider other processes that may control, or contribute to the control of, contaminant aqueous concentrations. In this respect, the concept of the solubility limit is useful to consider. Solubility control may allow contaminant concentrations to exceed those from a K_d model (if, for instance, sorption sites are inaccessible to the solution), or it may limit concentrations to levels below those from a K_d model. From the standpoint of predicting contaminant behavior to assess risk, if solubility limits that could lead to radionuclide concentrations higher than those derived from a K_d model are neglected, release rates may be underestimated.

This appendix reviews available data on solubility limits for selected radioelements in environments expected in SRS and INL cement-based disposal facilities covered by the Ronald W. Reagan National Defense Authorization Act of Fiscal Year 2005 (NDAA). This information will be useful in U.S. Nuclear Regulatory Commission (NRC) staff reviews of disposal facility performance assessments; the reviews are conducted as part of the NRC consultative role established by the NDAA.

1.2 Chemical Factors Affecting Solubility

In the context of water-solid interactions affecting contaminant release, solubility is a thermodynamic property of a solid substance in association with water. Solubility is the “total amount of the mineral that has dissolved at equilibrium” (Nordstrom and Munoz, 1994), that is, at saturation, usually expressed as a concentration such as moles of solute per liter of solution.

In modeling contaminant release, solubility is not defined as a property of an element. Rather, the solubility *limit* for an element is typically abstracted into models as a maximum concentration of that element. The solubility limit for an element is the aqueous concentration of the element in equilibrium with the solid (containing that element as a stoichiometric constituent) that limits the element to its lowest concentration. The solubility limit, therefore, is a property of an element—rather than of a solid phase—for a given set of physiochemical conditions (T, pH, solution composition).

The solubility of a solid is controlled by a reaction such as the following example for schoepite ($UO_3 \bullet 2H_2O$), a uranium mineral typically stable under oxidizing conditions (Murphy and Codell, 1999):

$$UO_3 \bullet 2H_2O + 2H^+ = UO_2^{2+} + 3H_2O \qquad (1\text{-}1)$$

In the presence of schoepite, the reaction in Eq. (1-1) defines the activity and, thus, the concentration of the dissolved uranyl ion (UO_2^{2+}) at equilibrium in terms of pH. Equilibrium aqueous reactions may also be written for the uranyl ion and other stable dissolved uranium species; for example

$$UO_2(CO_3)_2^{2-} + 2H = UO_2^{2+} + 2HCO_3^- \qquad (1\text{-}2)$$

The total mass of dissolved uranium (i.e., the solubility of schoepite) will include the masses of these other uranyl species in addition to the uranyl ion. Therefore, in the presence of schoepite, the dissolved uranium concentration is a function not only of the equilibrium reaction in Eq. (1-1), but also of other equilibria that may be sensitive to geochemical parameters such as pH and bicarbonate ion concentration [e.g., Eq. (1-2)]. Equilibrium constants for the various reactions are functions of temperature and pressure. The solubility of schoepite, then, is a function of several geochemical and physical variables and must be defined in those terms. Although a complete geochemical description is preferred for thermodynamic calculations, for discussion purposes it is often sufficient to define a few geochemical factors that most strongly influence solubility because of their presence in the solubility reaction or their impact on dissolved ionic species (e.g., pH, Eh, and carbonate species for schoepite in many systems).

Determination of the solubility limit for an element must also consider which solid phase is controlling the dissolved concentration. If there is another stable uranium mineral for which the solubility reaction results in lower uranium concentration than schoepite, that mineral will control the uranium concentration. This occurs because equilibrium with that other phase will prevent dissolved uranium from reaching a high enough concentration such that schoepite precipitates. Any additional uranium added to solution is consumed in precipitating the lower solubility uranium phase. Thus, thermodynamically defining a solubility limit involves both determining individual phase solubilities and choosing the appropriate solubility-limiting phase.

Release models do not necessarily assume that a given element will be released at its solubility limit. Other processes, such as coprecipitation and sorption, can limit concentration to a level lower than that constrained by solubility. Consequently, the solubility limit must be considered a maximum possible concentration; the release model may predict lower, even much lower, values [Table RAI–8–1 of DOE–Idaho (DOE–ID) (2006a) contains examples of K_d-based model

actinide concentrations lower than recommended solubility limits]. Likewise, it is possible that the solubility-limiting phase predicted from thermodynamic considerations may not readily form due, for example, to kinetic constraints. Using such a mineral could underpredict the radionuclide concentration. In this case, it may be preferable to select another mineral that, according to experimental studies, forms under the assumed conditions. In general, solubility limits must be evaluated for applicability to specific conditions and for the potential to both underpredict and overpredict concentration limits.

1.3 Predicting Solubility Limits Using Models and Experiments

Understanding the thermodynamic basis for solubility (Section 1.1) allows the use of models to predict radioelement solubility limits. The most common approach is to employ chemical equilibrium model codes [e.g., EQ3/6 (Wolery, 1992), Geochemist's Workbench® (Bethke, 1996), PHREEQC (Parkhurst, 1995)] to determine the saturation states of radioelement solid phases over a plausible range of solution chemistries. Once the least soluble solid phase is identified and it is deemed to be stable and likely to form under the conditions of interest, the radioelement aqueous concentration is calculated based on equilibrium with that phase and is established as the solubility limit. The results rely not only on the use of high-quality thermodynamic data, but also on assumptions regarding the attainment of equilibrium and the completeness of the list of solid phases included. Solubility limits may be expressed graphically as functions of important variables such as pH and f_{CO2} (which controls dissolved carbon species) so that possible variations in the environment may be understood.

Theoretical solubility models, which rely on assumptions regarding phase stability and equilibrium, must be evaluated in light of data from laboratory experiments designed to measure solubility limits. To be directly applicable to establishing radioelement solubility limits, these experiments should have the following characteristics:

- They should be designed to avoid interfering chemical reactions. For example, solubility studies of an actinide should exclude other actinides or major metals that may actively precipitate; otherwise, coprecipitation phenomena cannot be excluded. The presence or absence of colloids should be verified and any colloids present should be characterized.

- They should not be conducted in the presence of the waste form. Radioelement concentrations from waste form leaching or dissolution studies are useful for understanding radionuclide release, but they do not provide unambiguous solubility information. For example, sorption processes cannot be ruled out in the presence of a waste form substrate. For such experiments, concentrations must be considered to be minimum values for solubility limits.

- They should attempt to approach, in a controlled manner, solution-solid equilibrium from both oversaturation and undersaturation.

- In experiments approaching equilibrium from oversaturation, attempts should be made to identify the pure-phase solids that are precipitating the radioelement from solution.

While not all solubility studies will meet these criteria, they provide useful benchmarks with which to evaluate the data and their applicability to establishing solubility limits. The most useful approach is to evaluate solubility limits in light of a combination of thermodynamic model results, solubility experiments, and waste form experiments.

1.4 Selection of Elements for Review

The list of radioelements included in this review was adopted from the previous review of natural system sorption coefficient data for SRS and INL, and the basis for inclusion may be found there (Prikryl and Pickett, 2007). The main criterion was potential risk significance in groundwater pathway dose assessments. In the present review, radioelements will be subject to two levels of analysis, depending on consideration of both risk significance and the potential for solubility limits to be exceeded. Five radioelements—selenium, technetium, uranium, neptunium, and plutonium—were selected for more detailed solubility evaluation. All are potentially important in dose assessment models for SRS and INL. In addition, solubility limits for these elements are redox sensitive (i.e., aqueous speciation and solid phase stabilities may differ between oxidizing and reducing environments). Because oxidation-reduction potential is an important variable in understanding the evolution of cement-based waste environments at SRS and INL, these elements warrant closer solubility evaluation. Ten of the elements—carbon, nickel, strontium, niobium, tin, iodine, cesium, lead, americium, and curium—will be briefly discussed in terms of their solubility characteristics. These elements were assigned to this group on the following bases:

- Carbon, strontium, cesium, lead: Radioisotopes of these elements have very high specific activities, such that they will exist at very low mass levels in the waste form. Consequently, radioisotopes of these four elements will be unlikely to reach solubility limits in solution because of their own small mass and the likelihood that the element mass will be vastly dominated by nonradioactive isotopes. Among this list, strontium most prominently contributes to dose in NDAA-relevant assessments (e.g., sand pad release at INL; DOE–ID, 2006b).

- Nickel, niobium, tin, americium, and curium: Radioisotopes of these elements have moderate specific activities, but are still likely to have low mass contents in waste forms. Therefore, radioisotopes of these elements will be unlikely to reach solubility limits in solution. In the case of nickel, niobium, and tin, it is also likely that nonradioactive isotopes will dominate element mass. Furthermore, none of these elements have been identified as major dose contributors in NDAA-relevant assessments.

- Iodine: Radioactive I-129 is frequently identified as important to dose in NDAA-relevant groundwater dose assessments because of its high solubility limit and high mobility in groundwater as an anionic species. Because iodine is unlikely to reach saturation in solution in cement-based SRS and INL facilities, solubility control of iodine is not invoked in these assessments. Therefore, a detailed solubility evaluation is not necessary.

1.5 Approach To the Review

After first establishing the chemical characteristics of the waste form environment, including redox conditions (Section 2), this report will consider the five elements selected for detailed review (Section 3). Published experimental and modeling data will be discussed and additional solubility models dev eloped as necessary. Conclusions will be drawn regarding the likely range of solubility limits for the element under the defined range of conditions, considering the quality and applicability of the data and models. Next, the 10 elements chosen for less detailed evaluation will be discussed at a lower level of detail and without consideration of new models (Section 4). The summary and conclusions discussion (Section 5) will include consideration of the important data gaps and how they may be addressed in future studies. Unless specified otherwise, discussions of data and models apply at 25 °C.

2 CHEMICAL CONDITIONS RELEVANT FOR RELEASE FROM CEMENT-BASED WASTE FORMS

The main body of this report discusses the degradation evolution of cement-based materials, including evaluation of the state of knowledge of chemical changes over time (Glasser and Pabalan, 2007). The conclusions of those discussions, to which the reader is referred, will be used here to guide evaluation of the possible range in aqueous chemical conditions in contact with radionuclides in SRS and INL cement-based disposal environments.

2.1 Range of Expected Conditions In a Cementitious Environment

This scenario assumes that cement-based materials are eventually exposed to fluids with some communication with the external environment (Glasser and Pabalan, 2007). Cements will begin to degrade when exposed to carbonate-containing air and water. The key control on solution pH is evolution of cement phases in response to leaching. At the earliest stages, cement pore water will have pH between 12.5 and 14 (the elevation above 12.5 owing to the presence of soluble sodium and potassium). This stage is likely of short duration compared to succeeding stages because the alkalis will be leached by percolating water. Once alkalis are removed, relatively fresh cement will maintain a pore water pH of about 12.5 as long as portlandite is not exhausted. When portlandite dissolution is complete, leaching of amorphous to poorly crystalline calcium silicate hydrate (C-S-H) continues and the pH begins to decline to about 10.5. Up to this point, aqueous carbonate (important for actinide speciation and solubility) is likely to be relatively low as it is continually consumed by reaction with the alkaline constituents of the cement-based material to form various types of carbonate phases. Once C-S-H is exhausted, those carbonate phases, such as calcite, likely have become abundant and would control pH to around a value of 8. Aqueous carbonate concentration may then rise under the influence of atmospheric CO_2 gas.

At this point, it is assumed that, because of the large mass of degraded cement in tanks and monoliths at SRS and INL and because calcite is relatively insoluble compared to the cement phases, a pH of around 8 will be maintained in the pore water during the period of interest. This assumption is easily supported at INL, where groundwaters have pH values similar to 8 (see summary in Prikryl and Pickett, 2007). Groundwaters at SRS, however, are considerably more acidic, with typical ambient pH of less than 6 (Prikryl and Pickett, 2007) and low carbonate contents that would promote calcite dissolution. Note however, though, that the waste environment at SRS is in the unsaturated zone, such that the degraded material will be persistently exposed to carbon dioxide in air. Therefore, SRS groundwater chemistry may not provide an appropriate analog for waters contacting degraded cement in SRS facilities.

The oxidation-reduction potential of the pore water profoundly affect solubilities for the five elements selected for detailed review. Cements alone do not provide for a reducing chemical environment. DOE is expected to add blast furnace slag (BFS) to its grout mixtures to maintain a low Eh in the pore waters of the cement-based material. Thus, there is reason to expect that, through at least part of their history, cement-based materials in SRS and INL disposal facilities will be exposed to low-Eh conditions. Data are lacking, however, for predicting the long-term durability of those conditions. Radiolysis, for example, may contribute to generation of oxidizing species, and infiltration of environmental air and water will elevate Eh. We must, therefore,

consider scenarios in which oxidizing conditions are present in the waste as a result of the introduction of atmospheric oxygen.

2.2 Effects of Proposed DOE Formulations

As discussed elsewhere in this report, the expected DOE grout formulations for tank closure and Saltstone disposal will include ordinary Portland cement (OPC), fly ash, and BFS. In the long term, the latter two additives have implications for the Eh and pH evolution of the grout. As discussed in the previous section, slag can contribute to maintaining a reducing chemical environment. The main source of the reducing potential of slag is sulfide sulfur, which originates in the coke and ore used in iron processing and which is concentrated in the BFS. Thiosulfate, which may form from reaction between the slag sulfide and sulfur(VI) in Portland cement, may also contribute to the reduction capacity of the grout. Many uncertainties remain, however, regarding the long-term performance of slag-derived sulfur in poising Eh at low levels. In addition, it may not be possible to predict the initial sulfur content of the grout formulations.

Fly ash may contribute to reduction by the action of iron oxides and elemental carbon. Again, exact predictions of these effects are not possible because of a lack of long-term experimental data and potential variability in fly ash contents of these substances.

With regard to pH evolution, both fly ash and slag will most significantly affect grout by likely shortening the period of high pH buffering. This effect comes about through both dilution of portlandite and reaction between portlandite and the other components.

2.3 Effects of Residual Waste In Tank Heel In Contact With Grout

Any solubility effects of the residual material containing the radionuclides will depend on its abundance and solid phase chemistry. Very little information is available on the solid phases present in cleaned tank heels at SRS and INL. For SRS Tank 19, for example, the remaining solids after heel removal are described simply as 99.9 percent “inert chemicals” (DOE, 2005, p. 47) with radionuclides comprising the remaining volume. A similar description applies to Tank 18 (DOE, 2005, p. 60). In the case of Tanks 18 and 19, those solids are likely to be dominated by zeolite, but insoluble metal salts and oxides (chiefly of iron and aluminum) will also be present (Thomas, 2005a,b). Soluble materials appear to have been removed during the tank cleaning process. A survey of relevant INL documents did not reveal data on the specific solid phases present on the tank heel after cleaning (DOE–ID, 2006b, and references therein). The INL tank cleaning process, however, left behind very low masses of residual material. SRS is also studying more effective cleaning methods that may lead to very low residual masses.

It appears unlikely that the residual materials at the tank base will significantly affect the chemical environment for establishing solubility limits. This conclusion is based on: (i) the expected low masses of the residue and (ii) the removal of soluble materials from the residue during cleaning, leaving insoluble salts and oxides and silicates that will have a lesser impact on solution chemistry than the abundant overlying cement-based materials and their degradation products.

2.4 Summary of Expected Conditions

The chemical environment for release is controlled primarily by the evolution of the cement-based waste form or entombing grout. Solubility limits should be evaluated over the entire range considered feasible over 10,000 years. The solution pH is expected to range chiefly from approximately 12.5 (early) to 8 (late). To the extent that data are available, this report will also discuss data from the 12.5 to 14 pH range, which may characterize the earliest stages of cement-water interaction. The poising capacity afforded by BFS-cement blends (Section 5.3.1 of the main report) suggests that reducing conditions may dominate early on, with Eh likely poised to the range −200 to −350 mV. In isolation from air and in the absence of BFS, OPC would control Eh to around +80 mV (Angus and Glasser, 1985). A later oxidizing environment while portlandite is still present (pH ~12.5), with Eh of around +100 to +200 mV, cannot be ruled out if oxidizing unsaturated zone waters reach the cement. Under degraded conditions, atmospheric conditions may dominate, such that Eh could exceed +750 mV at pH 8 (using the expression of Langmuir, 1997, p. 409). Both reducing and oxidizing conditions, therefore, will be considered with respect to solubility limits. The Eh-pH field that encompasses these proposed conditions is illustrated by the shaded area in Figure 2-1. The timing of this chemical sequence depends on many factors, such as the availability of fast pathways that could cause more rapid degradation and oxidation.

2.5 Aqueous Conditions for Solubility Models

Solubility limits were calculated for selenium, technetium, uranium, neptunium, and plutonium at 25 °C using the SpecE8 and React components of Geochemist's Workbench Professional 6.0 (Bethke, 1996) with the thermo.com.v8.r6+.dat thermodynamic database. In the models, aqueous concentrations of these elements were set to be controlled by the pure solid phase that constrained the dissolved concentration to its lowest value (i.e., so that no pure phases were oversaturated). In a few cases documented in the following sections, certain phases were suppressed. For the lowest Eh runs, SpecE8 runs did not always converge. In those cases, it was necessary to use the "slide" capability in React in order to obtain equilibrium solution results over a range of Eh values. For plotting purposes, a value of 1 M was used when either no solubility control could be calculated or the calculated value was greater than 1 M. In these preliminary analyses, charge imbalance was not corrected.

Water compositions for solubility calculations were selected to span a range of conditions over the lifetime of a cement-based disposal environment (Table 2-1). For most compositions, a range of Eh values was simulated. While not all these solutions can be expected to directly reflect conditions in SRS or INL cement-based waste environments, they represent a inclusively broad range of chemistries. Solutions in contact with relatively fresh OPC (Waters 1, 3, and 16 in Table 2-1) are represented by (i) a model cement pore solution that has not interacted with groundwater (Berner, 2002, Table 2), (ii) a calculated solution composition resulting from groundwater reaction with a model cement solid assemblage (Glasser, et al., 1999, Table 6.39), and (iii) a measured OPC pore water chemistry (Angus and Glasser, 1985, Table III). Because Angus and Glasser (1985) did not report carbonate species, we have performed calculations both with no dissolved carbon and with a CO_3^{2-} concentration from the upper limit of Allard and Torstenfelt (1985). A substantial range in dissolved carbonate is, therefore, reflected in these waters. For each of these waters the model Eh range of −350 to +80 mV was taken from Angus

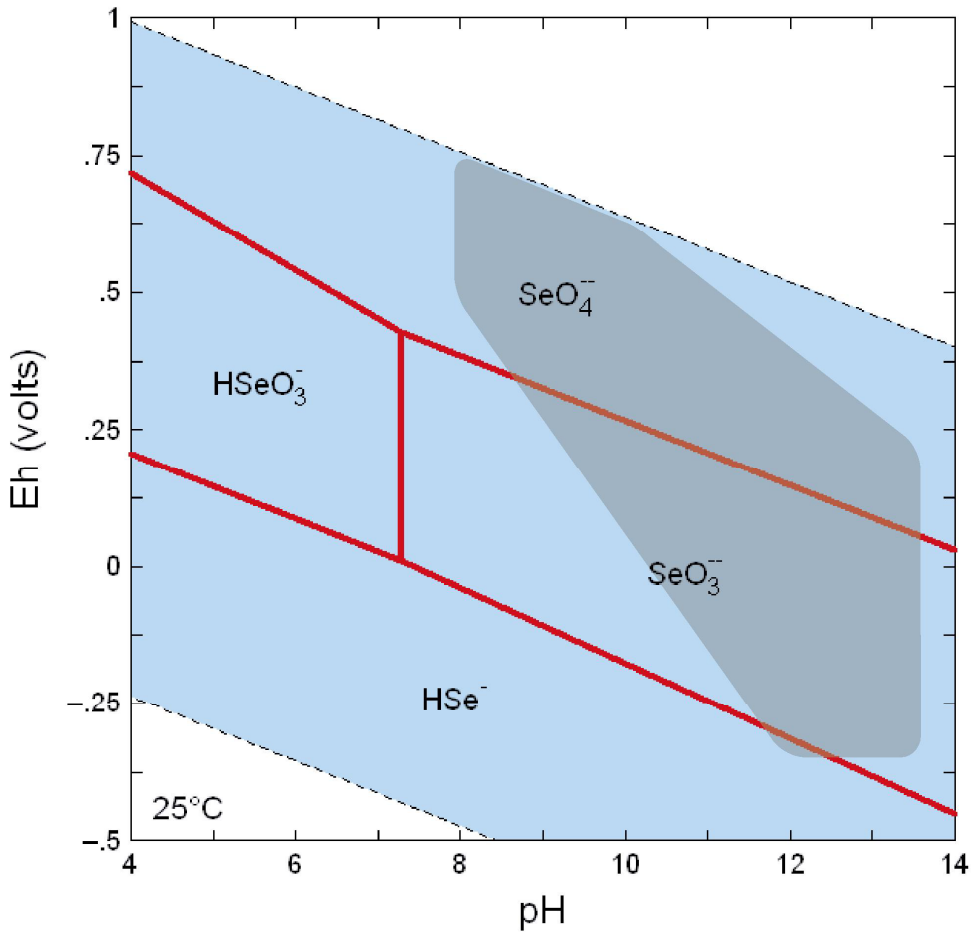

Figure 2-1. Eh-pH Stability Field for Water With a Shaded Area Representing the Approximate Range of Expected Conditions as Cement-Based Materials Degrade (Section 2.4). Aqueous Species Fields for Selenium Shown as an Example. Figure Produced Using Geochemist's Workbench Professional Version 6.0 With the thermo.comv8r6+.dat Database.

and Glasser (1985); note that, although a reducing agent such as sulfide in BFS is needed to reach the low end of the Eh range, these three pore water chemistries do not reflect the chemical contributions of such an agent

Solutions in contact with a relatively fresh blend of OPC and BFS (Waters 4, 7, and 8) are represented by (i) a calculated pore water for a 75-percent BFS blend that has interacted with a saline water (Glasser, et al.,1999, Table 6-41), (ii) a measured water equilibrated with a blend of BFS, OPC, and limestone aggregate at a ratio of 7:2:19 (Berry, et al., 1989, Table 2), and (iii) a calculated pore water resulting from equilibration of pure water with a 75-percent BFS blend (Glasser, et al., 1999, Table 6.40). These three solutions have lower pH (11.9 to 12.3) than the "initial stage" solutions discussed in the previous paragraph, and a higher upper limit for Eh of +200 mV was assumed.

Table 2-1. Water Compositions Selected for Solubility Limit Calculations

	Water 1	Water 2	Water 3	Water 4	Water 5	Water 6	Water 7	Water 8
pH	13.44	12.5−5	13.4	12.2	12.5	10.5	11.88	12.28
Na+ (mol/L)	0.101	0.169	0.363	0.363			4.4e−04	
K+ (mol/L)	0.303	0.0057	0.0039	0.0039				
Mg++ (mol/L)	1.3e−08	1e−07	7.43e−11	9e−10				1.42e−08
Ca+(mol/L)+	8.43e−04	0.0201	5.62e−04	8.53e−04	0.02	0.002	2.2e−03	1.28e−02
Al+++ (mol/L)	1e−05	5e−06	1.54e−03	1.74e−04			1.7e−04	1.96e−05
Cl− (mol/L)		0.16	2.74e−02	2.47e−04				
F− (mol/L)	7.6e−04	1e−04						
CO3−− (mol/L)	2.04e−04	1e−05	4.42e−02	3.76e−05		Control by calcite, given Ca++	1.1e−04	
SO4−− (mol/L)	7.5e−04	1e−04	2.35e−04	5.56e−04	0.001 and 0.02	0.001		4.89e−06
H2SiO4−− (mol/L)	5e−05	1.6e−05	3.23e−04	2.73e−04	1e−04		1.3e−04	8.4e−06
Eh	−350 mV to +80 mV	−350 mV to +200 mV	−350 mV to +80 mV	−350 mV to +200 mV	−350 mV to +200 mV	0 mV to +600 mV	−350 mV to +200 mV	−350 mV to +200 mV
	Berner (2002, Table 2)*	Wieland and Van Loon (2003), Table 3)†	Glasser, et al. (1999, Table 6.39)‡	Glasser, et al. (1999, Table 6.41)‡	Berner (1992, Figures 1–3)§ and Atkins, et al. (1991)‖	Berner (1992, Figures 1-3)§ and Atkins, et al. (1991)‖	Berry, et al. (1989, Table 2)¶	Glasser, et al. (1999, Table 6.40)‡
	Water 14	**Water 16**	**Water 19**	**Water 25**	**Water 26**	**Water 27**	**Water 29**	**Water 30**
pH	12.49	13.4	11.00	10.02	9.16	5.8	8.1	8.27
Na+ (mol/L)	8.8e−05	0.058				8.6e−05	3.57e−04	
K+ (mol/L)	2.2e−05	0.222				3.2e−05	4.09e−05	
Mg++ (mol/L)						2.3e−05	5.76e−04	
Ca++ (mol/L)	2.2e−02	2.7e−03	0.001	0.00197	9.3e−04	1.7e−04	1.10e−03	4.97e−04
Al+++ (mol/L)								
Cl− (mol/L)						1.3e−04	2.09e−04	
F− (mol/L)	7.5e−05					32.e−06		
CO3−− (mol/L)	6.5e−05	Zero and 3e−06	Control by calcite	Control by calcite	Control by calcite	2.6e−04	3.39e−03	9.86e−04
SO4−− (mol/L)	5.0e−04					1.1e−05	2.29e−04	
H2SiO4−− (mol/L)	1.0e−05			0.00387	0.00260		3.00e−04	

Table 2-1. Water Compositions Selected for Solubility Limit Calculations (continued)

	Water 14	Waster 16	Water 19	Water 25	Water 26	Water 27	Water 29	Water 30
Eh	−350 mV to +200 mV	−350 mV to +80 mV	−100 mV to +500 mV	0 mV to f(O2) = 0.2	+100 mV to f(O2) = 0.2	Dissolved oxygen = 9 mg/L	+750 mV	f(O2) = 0.2
	Berner (1999, Table 8)#	Angus and Glasser (1985, Table III)** and Allard and Torstenfelt (1985)††	Bradbury and Sarott (1995)‡‡	Greenberg and Chang (1965)§§	Greenberg and Chang (1965)§§	Prikryl and Pickett (2007, Table 2-1)‖‖	Del Debbio and Thomas (1989)¶¶	Equilibrium dissolution of calcite in equilibrium with air, using EQ3/6 Version 7.2b

*Berner, U. "Project Opalinus Clay: Radionuclide Concentration Limits in the Cementitious Near-Field of an ILW Repository." PSI Bericht 02-26, Nagra NTB 02-22. Villigen, Switzerland: Paul Scherrer Institute. 2002.
†Wieland, E. and L.R. Van Loon. "Cementitious Near-Field Sorption Data Base for Performance Assessment of an ILW Repository in Opalinus Clay." PSI Bericht 03-06. Villigen, Switzerland: Paul Scherrer Institut. 2003.
‡Glasser, F.P., M. Tyrer, K. Quillin, D. Ross, J. Pedersen, K. Goldthorpe, D.G. Bennett, and M. Atkins. "The Chemistry of Blended Cements and Backfills Intended for Use in Radioactive Waste Disposal." R&D Technical Report P98. Bristol, United Kingdom: U.K. Environment Agency. 1999.
§Berner, U.R. "Evolution of Pore Water Chemistry During Degradation of Cement In a Radioactive Waste Repository Environment." *Waste Management*. Vol. 12. pp. 201–219. 1992.
‖Atkins, M., F.P. Glasser, and L.P. Moroni. "The Long-Term Properties of Cement and Concretes." *Scientific Basis for Nuclear Waste Management XIV*, T. Abrajano, Jr. and L.H. Johnson, eds. Materials Research Society Symposium Proceedings. Vol. 212. pp. 373–386. Pittsburgh, Pennsylvania: Materials Research Society: 1991.
¶Berry, J.A., J. Hobley, S.A. Lane, A.K. Littleboy, M.J. Nash, P. Oliver, J.L. Smith-Briggs, and S.J. Williams. "Solubility and Sorption of Protactinium in the Near-Field and Far-Field Environments of a Radioactive Waste Repository." *Analyst*. Vol. 114. pp. 339–347. 1989.
#Berner, U. "Concentration Limits in the Cement Based Swiss Repository for Long-Lived, Intermediate-Level Radioactive Wastes (LMA)." PSI Bericht 99-10. Villigen, Switzerland: Paul Scherrer Institut. 1999.
**Angus MJ and FP Glasser. "The Chemical Environment in Cement Matrices." *Scientific Basis for Nuclear Waste Management IX*. L.O. Werme, ed.. Materials Research Society Symposium Proceedings. Vol. 50. pp. 547–556. Pittsburgh, Pennsylvania: Materials Research Society: 1985
††Allard, B. and B. Torstenfelt. "Actinide Solubilities and Speciation in a Repository Environment." Technical Report NTB 85-18. Baden, Switzerland: NAGRA. 1985.
‡‡Bradbury, M.H. and F.-A. Sarott. "Sorption Databases for the Cementitious Near-Field of a L/ILW Repository for Performance Assessment." PSI Bericht 95-06. Villigen, Switzerland: Paul Scherrer Institut. 1995.
§§Greenberg, S.A. and T.N. Chang. "Investigation of the Colloidal Hydrated Calcium Silicates II. Solubility Relationships in the Calcium Oxide–Silica–Water System at 25 °C." *Journal of Physical Chemistry*. Vol. 69. pp. 182–188. 1965.
‖‖Prikryl, J.D. and D.A. Pickett. "Recommended Site-Specific Sorption Coefficients for Reviewing Non-High-Level Waste Determinations at the Savannah River Site and Idaho National Laboratory." San Antonio, Texas: CNWRA. 2007.
¶¶Del Debbio, J.A. and T.R. Thomas. "Transport Properties of Radionuclides and Hazardous Chemical Species in Soils at the Idaho Chemical Processing Plant." WINCO–1068. Idaho Falls, Idaho: Westinghouse Idaho Nuclear Company, Inc. 1989.

The next category of pore water simulations (Waters 2, 5, and 14) represents the stage of cement degradation when portlandite is the chief cement phase, pH is about 12.5, and C-S-H gels have begun to form, corresponding, for example, to Region II of Bradbury and Sarott (1995). These waters, which do not explicitly account for OPC content, are represented by (i) a "Stage II" model water resulting from groundwater interaction with cement (Wieland and Van Loon, 2003, Table 3), (ii) a simplified calcium-silica water reflecting the earliest, high-Ca/Si stages of C-S-H evolution (Berner, 1992, Figures 1–3) with a sulfur content based on Atkins, et al. (1991), and (iii) a model portlandite-saturated solution (Berner, 1999, Table 8). Eh was varied between −350 and +200 mV to simulate a range of redox conditions.

A set of five waters (6, 19, 25, 26, and 30) represents progressive carbonation and C-S-H degradation (and decreasing Ca/Si) as the buffering capacity of cement constituents declines. Specific water chemistries used in models are (i) a simplified calcium-silica water reflecting the latest, low-Ca/Si stages of C-S-H evolution (Berner, 1992, Figures 1–3), with a pH of 10.5, a sulfur content based on Atkins, et al. (1991), and dissolved carbonate controlled by calcite solubility; (ii) a simplified pH 11, calcite-saturated water based on the Bradbury and Sarott (1995) description of Region III; (iii) a simplified pH 10, calcite-saturated predominantly Ca-Si water based on measurements by Greenberg and Chang (1965) used in the models of Berner (1992); (iv) a simplified pH 9, Ca-Si, calcite-saturated water based on experimental measurements by Greenberg and Chang (1965) used in the models of Berner (1992); and (v) a model water representing calcite dissolution in pure water in equilibrium with the atmosphere. Eh ranges selected for these waters reflect variation from mildly oxidizing to equilibrium with atmospheric oxygen.

Finally, as end members, solubility limits were calculated for groundwaters from the INL and SRS sites with the implicit assumption that the grout waste form has become essentially unreactive with percolating waters. Constituent values for Water 27 represent midpoints of the range presented for the Upper Three Runs aquifer upper zone at SRS in Prikryl and Pickett (2007, Table 2-1). As mentioned in Section 2.1, there is no particular reason to expect that this specific water will be present in the SRS unsaturated zone, but it is an oxidizing water and may reflect to a degree geochemical influences of the SRS subsurface. Composition 29 is a perched water sampled from the INL unsaturated zone (Del Debbio and Thomas, 1989).

3 DETAILED SOLUBILITY REVIEWS

This section contains detailed discussions of solubility limits for selenium, technetium, uranium, neptunium, and plutonium under the established range of conditions. Both experimental and modeling results will be addressed, and conclusions will be drawn concerning how consideration of solubility limits affects evaluation of radionuclide release models. New solubility models will be presented using the representative waters of Table 2-1 over a range of Eh values. Useful context for these discussions is provided by Kaplan (2006): a recent compilation of recommended geochemical parameters for use in modeling radionuclide release and transport at SRS sites, including the Saltstone facility. Kaplan (2006) did not explicitly address grouted tanks, but the solubility data discussed may also be applicable to the cementitious tank environment. Compared to the present report, the Kaplan (2006) analysis established "apparent solubility concentration limits" that did not necessarily reflect true solubility, but could also incorporate the effects of other processes such as coprecipitation or sorption. While that is a legitimate approach to developing model parameters, the present report is concerned with pure-phase solubility as a control on limiting concentration.

3.1 Selenium

The fission product Se-79 is a potentially mobile constituent of cement-based wastes at SRS and INL. Figure 3-1 shows an Eh-pH plot of dissolved selenium species. The shaded field on the plot is an approximate representation of the range of expected conditions in the presence of a degrading slag-cement blend. It is assumed that as portlandite and C-S-H degrade and pH decreases, the reducing capacity of the material will also decrease as contact with oxidizing waters increases and sulfide is removed. Therefore, the slag-cement field tends to higher Eh with lower pH as degradation proceeds.

Figure 3-1 shows that, under strongly oxidizing aqueous conditions at pH >8, selenium is present in the hexavalent state as the selenate (SeO_4^{2-}) anion (Berner, 1999; Séby, et al., 2001; Berner, 2002; Krupka, et al., 2004). Under moderately oxidizing and reducing conditions, tetravalent selenium as the selenite (SeO_3^{2-}) anion predominates. At a given pH, progressively more strongly reducing waters favor the −2 valence state HSe^- anion, but Figure 3-1 suggests that these conditions are unlikely in the environment being considered.

At the lowest Eh values considered, it is possible that crystalline elemental Se^0 solubility may limit dissolved selenium to 10^{-4} M or less (Séby, et al., 2001; Kitamura, et al., 2004; Iida, et al., 2001. The Se^0 stability field, however, is not within the assumed Eh-pH region. Throughout the aqueous selenite and selenate stability field (Figure 3-1), selenium solubility-limiting phases are more likely to be metal selenates or selenites.

Kaplan (2006) assumed no solubility control of selenium under both oxidizing and reducing cementitious conditions.

3.1.1 Experimental Data

Few selenium phase solubility studies have focused on cementitious conditions. Bayliss, et al. (1992) measured $FeSe_2$ solubility in cement-equilibrated water at pH 12.2. For Eh of −405 mV,

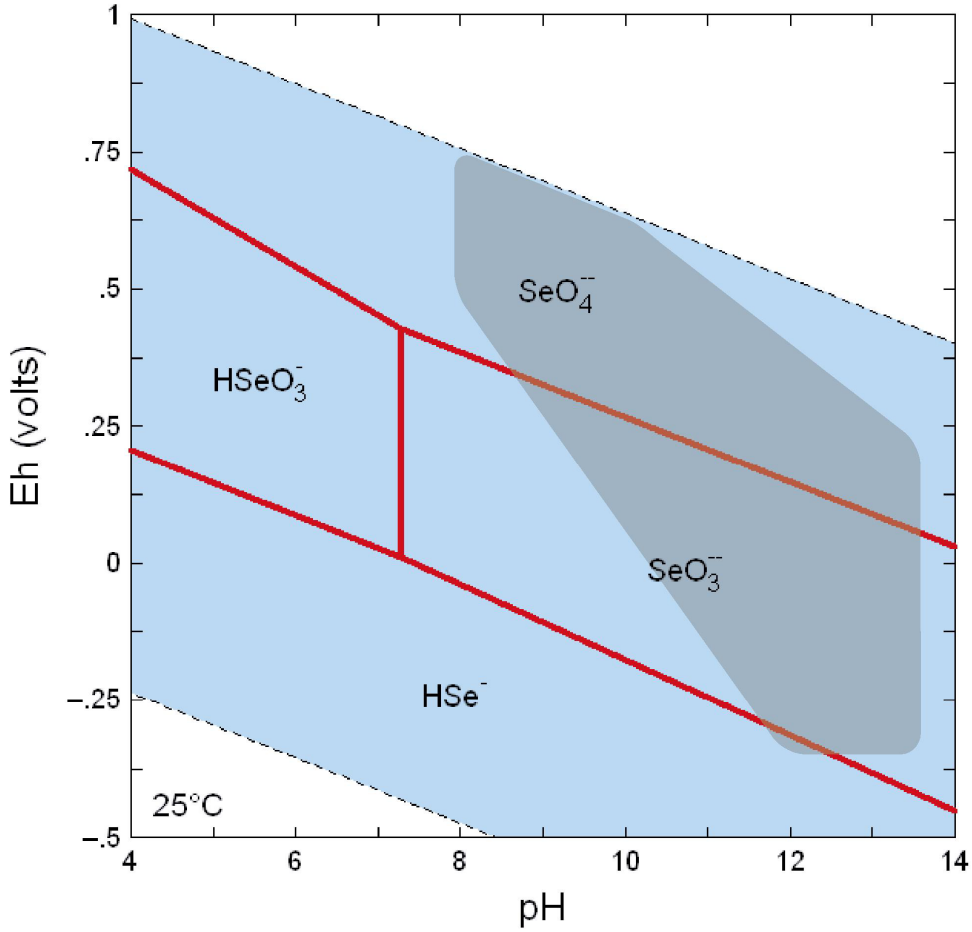

Figure 3-1. Eh-pH Stability Fields for Aqueous Selenium (1×10^{-8} M) in Pure Water at 25 °C (Solids Suppressed) Calculated Using Geochemist's Workbench Version 6.0 With the thermo.com.v8.r6+.dat Database. The Shaded Area Represents the Approximate Range of Expected Conditions as Cement-Based Materials Degrade (Section 2.4). Addition of Carbon or Sulfur Does Not Alter the Aqueous Species Fields. The Blue Field Defines Water Stability.

the aqueous selenium concentration, predicted to be HSe^-, was 9×10^{-8} to 5.0×10^{-7} M. There were no measurements at higher Eh, which may be more applicable to the assumed conditions (Figure 3-1). Kitamura, et al. (2004) measured crystalline Se^0 solubilities of up to 10^{-4} M at pH from 11 to 13. Although the expression they derived for Se^0 solubility predicts a dissolved selenite anion concentration of only 3×10^{-9} M at pH 12 and Eh −350 mV, the predicted solubility quickly increases as pH or Eh increases. Iida, et al. (2001) also measured Se^0 solubility at high pH and low Eh, but the measurements at pH above 12 were all at Eh below −385 mV. Extrapolated to higher Eh, the dissolved concentrations of their model SeO_4^{2-} ion are very low, but are likely to be less than the concentration of selenite in solution. Taken together, these studies show that elemental Se^0 has low solubility at the boundary of the assumed Eh-pH region, but will not control dissolved selenium to low values through most of that region.

Séby, et al. (2001) discuss a broad range of experimental data aimed at elucidating thermodynamic properties of selenium substances. These data were not aimed specifically at understanding solubility limits in a cementitious environment. No low-solubility selenate likely to form in a cementitious environment is evident from the data in Séby, et al. (2001). Solubility control of dissolved selenium, therefore, is unlikely in the selenate stability field. Calcium selenite ($CaSeO_3$, $CaSeO_3 \bullet H_2O$, or $CaSeO_3 \bullet 2H_2O$), however, may be an important phase in the presence of cement, and the data on this phase from Séby, et al. (2001) will be used in the following section on selenium solubility models.

3.1.2 Models

Chemical models consistently yield high selenium solubility limits under oxidizing conditions (e.g., Berner, 2002). There is the possibility, however, for the presence of solubility-limiting phases at lower Eh. When Berner (2002) calculated the selenium solubility limit at pH 12.6, Eh −230 mV, and 25 °C using the Nagra/PSI chemical thermodynamic database, he obtained a concentration of about 0.1 M due to Se^0 [or Se(cr), using his terminology] control. He argued, however, that this result was a function of the presence of Se^0 as the only selenium solid phase in the database. Based on data from Séby, et al. (2001), Berner (2002) proposed $CaSeO_3 \bullet H_2O$ as the solubility limiting phase, assumed an aqueous Ca^{2+} concentration of 2×10^{-2} M, and calculated a solubility of 1.1×10^{-5} M at the given conditions. A higher value of 7×10^{-4} M was obtained at pH 13.4 as a result of a lower assumed Ca^{2+} concentration. Berner (2002) used the $CaSeO_3 \bullet H_2O$ solubility data of Sharmasarkar, et al. (1996), as reported in Séby, et al. (2001), for these calculations. If we take the Sharmasarkar, et al. (1996) solubility product for $CaSeO_3 \bullet H_2O$ of $10^{-7.76}$, assume activity coefficients of one, and use the Angus and Glasser (1985) Ca^{2+} cement pore water concentration of 2.7×10^{-3} M, we obtain a dissolved SeO_3^{2-} concentration of 6×10^{-6} M.

New selenium solubility calculations were performed for this report using the representative waters discussed in Section 2.5. Preliminary results are plotted in Figure 3-2; for some water compositions, results for a number of different modeled Eh values are shown. The lowest solubility-limited selenium concentrations (3 to 8×10^{-8} M) correspond to Eh −350 mV at pH 11.9 to 12.6; in this pH range, calculated solubility limits rise rapidly as Eh rises. At pH 13.4 (fresh OPC) and Eh −350 mV, values are much higher—greater than 7×10^{-3} M—and again rise rapidly with Eh. At all pH values less than 11, solubilities are greater than 0.05 M, with lack of solubility control below 1 M being typical for elevated Eh waters that would result from atmospheric influence. In general, with increasing Eh, the solubility-limiting model solid changes from metallic Se^0 to $CaSeO_3 \bullet 2H_2O$ to $CaSeO_4$.

The new preliminary calculations agree with existing models and the experimental data discussed in Section 3.1.1, indicating solubility controls selenium concentrations to low values only around pH 12 to 12.5 and lowest Eh. For other pH values (including 13.4) and Eh greater than about −250 mV, selenium solubilities will exceed 0.05 M. Values above 1 M are typical for Eh > +100 mV.

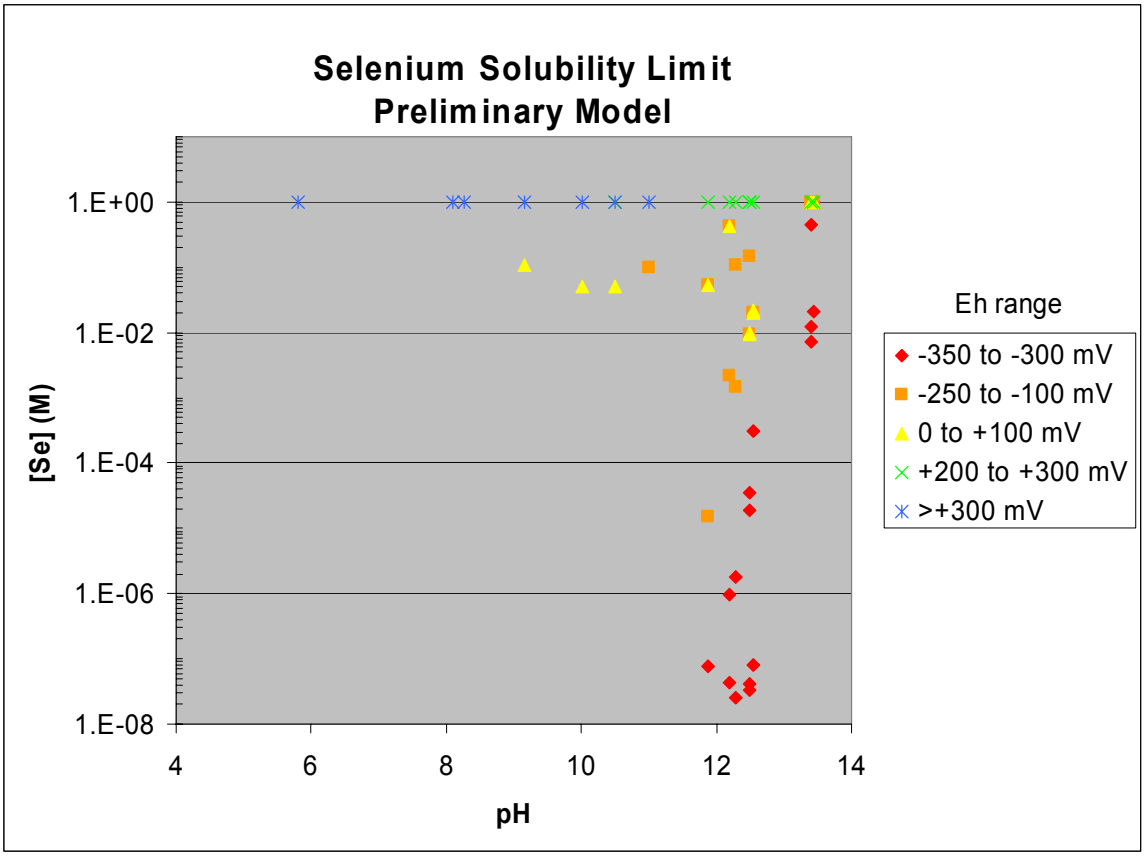

Figure 3-2. Preliminary Results of Selenium Solubility Limit Model Calculated Using Geochemist's Workbench Version 6.0 (SpecE8 and React Modules) With the thermo.com.v8.r6+.dat Thermodynamic Database. Model Values Are for Representative Waters in Table 2-1, With a Range of Selected Eh Values Illustrated for Most Compositions.

3.1.3 Conclusions

The experimental and modeling data suggest that, through most of the pH-Eh region of interest (Figure 3-1), selenium will not be limited to low concentrations by pure solid-phase solubility. At pH of about 12.5 and the lowest Eh of −350 mV (i.e., the lower left of the outlined field in Figure 3-1), it is possible that calcium selenite solubility will limit dissolved selenium to below about 10^{-4} M. The supporting thermodynamic data, however, are sparse and contradictory. There is also a possibility of Se^0 control of low dissolved concentration in this same portion of pH-Eh range. For both phases, however, solubilities rise markedly as conditions deviate from this subregion. Therefore, solubility control should be applied for selenium only if pH-Eh conditions can be confidently confined to lowest Eh when pH is around 12.5. As this report's discussions of chemical conditions suggest, there is limited confidence in the durability of these conditions. The conservative approach, therefore, remains to assume no selenium solubility control.

3.2 Technetium

Like selenium, technetium solid phase and aqueous species stabilities are strong functions of pH and Eh due to a range of feasible oxidation states (see discussion in Krupka, et al., 2004). The desire to limit technetium release from cement-based waste forms by reducing mobile Tc^{VII}) to Tc^{IV} is a key motivation for the use of reducing agents such as BFS (see Section 5.6 of the main report). Under aqueous oxidizing conditions, the pertechnetate anion TcO_4^- dominates and solubility limiting pertechnetate solids are not expected to form. The Eh-pH stability region for pertechnetate is quite large (Figure 3-3). Under more reducing conditions, the aqueous speciation of Tc^{IV} may be dependent on the abundance of carbonate (Krupka, et al., 2004), but these carbonate species were not present in the database used for the Figure 3-3 calculations. In the presence of sulfide (a presumed slag ingredient) at low Eh, technetium solubility may be controlled to low levels by formation of Tc^{IV} sulfides such as TcS_2 and Tc_3S_{10} (Lukens, et al., 2005). Hydrous oxides may also have an impact on solubility. Therefore, the key issue for technetium solubility is whether the conditions under which Tc^{IV} sulfides or other insoluble Tc^{IV} solids will form are attained and maintained in grout.

For the period when initial reducing conditions are maintained in cement-based material, Kaplan (2006) proposed a "reasonably conservative" technetium solubility limit of 10^{-9} M and a "best," or expected, value of 10^{-10} M. The range Kaplan (2006) considered included highly degraded conditions when the pH is 5.5—the same as local SRS groundwater. There is no reason to expect that, in the vadose zone setting of the waste tanks and Saltstone monolith, reducing conditions would be maintained in the presence of groundwater (which, in any case, may not have such low pH). No solubility limit would be used once oxidizing conditions are encountered.

3.2.1 Experimental Data

Krupka, et al. (2004) provided a useful overview of the technetium experimental literature, which will not be detailed here. Pilkington (1990) measured technetium concentrations of around 10^{-7} M in cement-equilibrated solutions at an Eh of −450 mV, but solid phases were not identified. Greenfield, et al. (1998) also measured technetium solubility in cement-equilibrated water at pH 12.3 and low Eh (−520 to −510 mV), obtaining concentrations between 4×10^{-9} and 1×10^{-8} M. These studies assumed that the solubility-limiting phase was Tc^{IV} oxide or its hydrated forms ($TcO_2 \bullet xH_2O$). Lee and Bondietti (1983) identified technetium sulfide solids that formed under reducing conditions in ferrous solutions (not cementitious) and the formula Tc_2S_7 was adopted, but never fully verified, for a solubility-limiting Tc^{VII} phase that could form in sulfide-containing cements. Recently, Lukens, et al. (2005) identified the technetium solid forming in sulfide-containing cements as a Tc^{IV} phase with the formula Tc_3S_{10}. Lukens, et al. (2005) did not measure the solubility of this phase or define its stability limits in terms of pH and Eh. Much of the technetium experimental literature is concerned with leaching or sorption behavior and is, therefore, not directly applicable to solubility determination.

3.2.2 Models

Thermodynamic models have often been employed in attempts to predict technetium release behavior (e.g., Smith and Walton, 1993; Westinghouse Savannah River Company, 1992; Greenfield, et al., 1998; Krupka and Serne, 1998; Berner, 2002; Krupka, et al., 2004). Berner

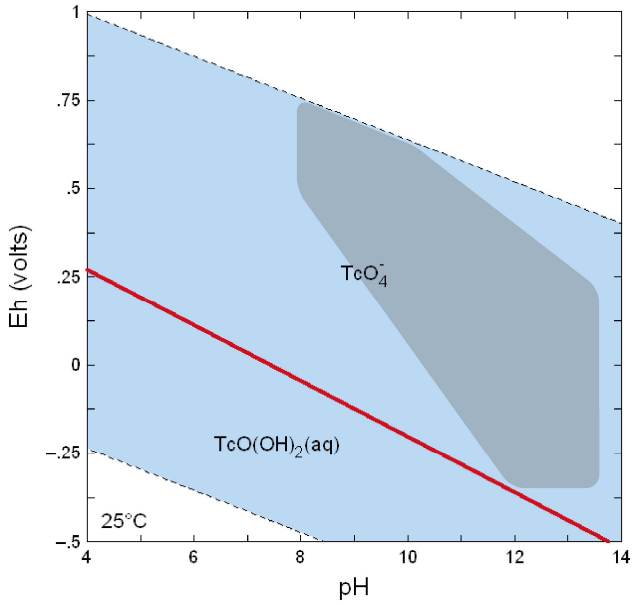

Figure 3-3. Eh-pH Stability Fields for Aqueous Technetium (1×10^{-8} M) in Pure Water at 25 °C (Solids Suppressed) Calculated Using Geochemist's Workbench Version 6.0 With the thermo.com.v8.r6+.dat Database. The Shaded Area Represents the Approximate Range of Expected Conditions as Cement-Based Materials Degrade (Section 2). Addition of Carbon or Sulfur Does Not Alter the Aqueous Species Fields. The Blue Field Defines Water Stability.

(2002) predicted a solubility limit, controlled by $TcO_2 \bullet xH_2O$, of around 10^{-5} M at an Eh of −350 mV for cement pore water; the model solubility limit rose two orders of magnitude at −300 mV. Krupka and Serne (1998) calculated a Tc_3O_4 solubility of 6×10^{-6} M at pH 12.5 and Eh −267 mV. Krupka, et al. (2004) showed model results on an Eh-pH plot that suggested solubility control by $TcO_2 \bullet 2H_2O$(am) to 10^{-7} M in the ranges pH 12 to 14 and Eh −350 to −500 mV. At higher pH and Eh, TcO_4^- anion was stable and solubility was not limited. In an early performance assessment for the Saltstone facility, WSRC (1992) calculated a technetium solubility limit of 10^{-20} M for a sulfide-rich cement pore fluid chemistry at pH 14. The solubility-limiting solid was heptavalent Tc_2S_7; the authors conceded that the result was highly uncertain. Clearly, the experimental and modeling data show the potential for low technetium solubility limits under the assumed conditions. These various results, however, illustrate the difficulty in predicting technetium phase solubilities at high pH and low Eh.

Indeed, thermodynamic data on technetium in this pH/Eh range are highly uncertain and limited in scope (Rard, et al., 1999). Thermodynamic values for hydrated Tc^{IV} oxides are not well constrained, and even the existence of the Tc_2S_7 phase has been questioned (Lukens, et al, 2005). In their geochemical review for Hanford disposal facilities, Krupka, et al. (2004, p. 3.24) stated:

> Although the thermodynamic stability of TcO_4^- is well established, thermodynamic data for other aqueous complexes and solids containing technetium in its various valence states are extremely limited. The absence of such data precludes the use of thermodynamic calculations to evaluate the

environmental behavior of reduced species of dissolved technetium with respect to pH, Eh, and the presence of important dissolved complexing ligands such as dissolved phosphate, sulfate, chloride, and others.

New equilibrium technetium solubility models were performed using the representative waters discussed in Section 2.5. Preliminary results are plotted in Figure 3-4; for some water compositions results for a number of different modeled Eh values are shown. For these models, precipitation of $KTcO_4$ and Tc_3O_4 was suppressed; these phases typically limited solubility in initial runs but have not been identified from experiments. A pattern similar to selenium emerges from Figure 3-4. Very low solubilities were calculated only at pH 11.9 to 12.6, reaching as low as 2×10^{-13} M at −350 mV. Calculated solubility limits rise markedly as Eh rises to −200 mV and, in any case, the calculated solubility limiting phases for these low concentrations, such as $Tc(OH)_2$ and $Tc(OH)_3$, are also unsubstantiated by experiments. (Notably, the proposed sulfide Tc_2S_7 did not approach saturation in any runs that included sulfur.) At pH 13.4, technetium solubilities exceed 7×10^{-5} M, with low values being obtained only at −350 mV. For all pH below 11.9 and all Eh above −200 mV, technetium was not limited to below 1M.

The preliminary models did not predict precipitation of any expected technetium solids (e.g., $TcO_2 \bullet H_2O$), but did conform to the pattern established in laboratory and previous modeling studies. Technetium solubility appears to be limited only at Eh of −200 mV and lower, particularly for the 12 to 12.5 pH range. At higher pH, solubility is limited only at Eh below −300 mV and, at lower pH, is not limited at all.

3.2.3 Conclusions

For the present case, the pessimistic view of solubility modeling and the scarcity of experimental data are compounded by the fact that the lower Eh-pH range of interest lies in the proximate boundary between the stability fields of Tc^{VII} and Tc^{IV} (Figure 3-3). In addition, both the reducing capacity of the slag-cement mixture and the formation of potentially solubility-limiting technetium sulfides are dependent on the initial sulfide content and its temporal evolution. In light of these uncertainties and the dominance of Tc^{VII} species as Eh rises with the introduction of atmospheric oxygen, it is prudent to assume that no technetium solubility-limiting phases will form in the cementitious environment. This conclusion could be altered if low-Eh conditions could be more confidently predicted.

3.3 Uranium

A key geochemical feature of uranium is its redox sensitivity. Under oxidizing conditions, the relatively mobile U^{VI} oxidation state dominates, whereas U^{IV} dominates under reducing conditions. In the pH range 8 to 14, uranium aqueous speciation and, thus, solubility limits are strongly controlled by dissolved carbonate. Figures 3-5 and 3-6 compare calculated uranium aqueous speciation in a carbonate-free system and in a system in equilibrium with atmospheric CO_2. It is not expected that such CO_2 activity will apply during the high-pH period when CO_2 will be consumed by carbonation reactions with cement phases; the assumed carbon conditions are for comparative purposes only. For the Eh-pH region of interest (shaded area in Figure 3-6),

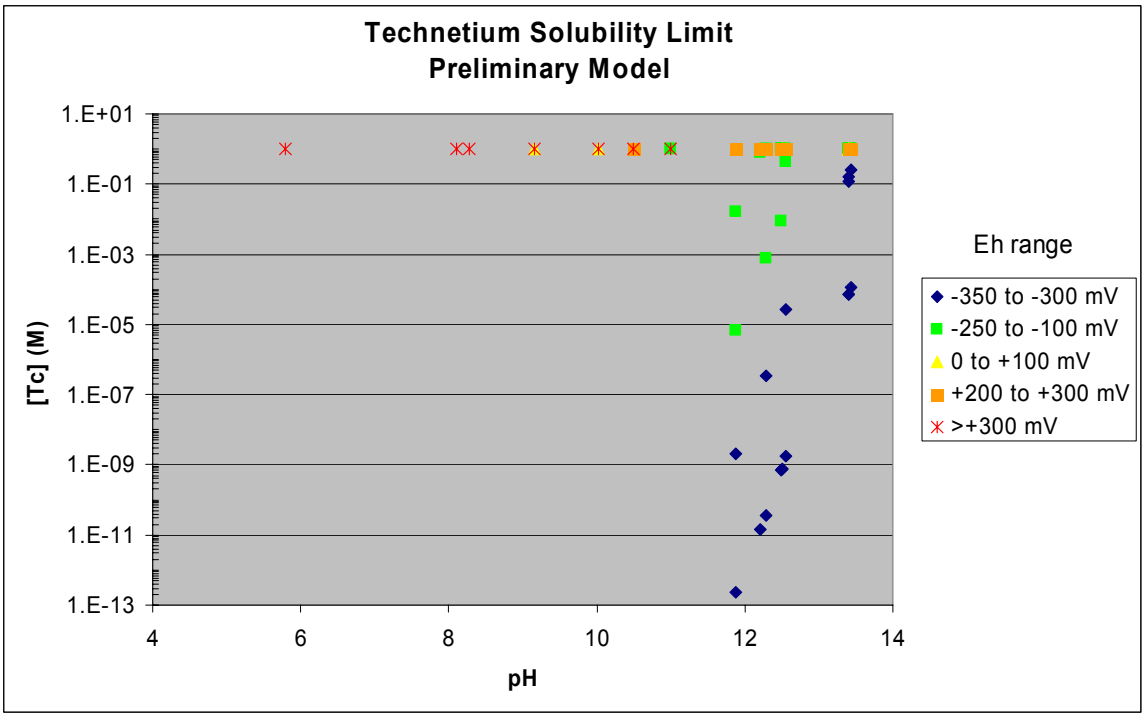

Figure 3-4. Preliminary Results of Technetium Solubility Limit Model Calculated Using Geochemist's Workbench Version 6.0 (SpecE8 and React Modules) With the thermo.com.v8.r6+.dat Thermodynamic Database. . Model Values Are for Representative Waters in Table 2-1, With a Range of Selected Eh Values Illustrated for Most Compositions.

CO_2 will promote the formation of U^{VI} anionic carbonate species, which reduced the $U^{IV}(OH)_5^-$ field and may stabilize higher dissolved uranium concentrations. [These observations are not, in general, affected by using the models of Langmuir (1997), in which the $U(OH)_5^-$ field is absent and a different U^{VI} carbonate complex dominates in the field of interest.] It is possible, therefore, that low-solubility U^{IV} solid phases may be unstable under most of the conditions of interest.

For young cement under reducing conditions (pH 12.5), Kaplan (2006) recommended uranium solubility limits of 5×10^{-5} M and 10^{-6} M as conservative and best values, respectively. For moderately aged (pH 10.5) and aged cements, Kaplan (2006) proposed corresponding limits of 5×10^{-6} M and 10^{-7} M. For oxidizing conditions, the young and moderately aged cement conservative and best values were 5×10^{-6} M and 10^{-7} M, respectively, while the corresponding values for aged cement were 5×10^{-5} M and 10^{-6} M. Note that for Kaplan (2006), "aged" conditions assumed a pH of 5.5, corresponding to local groundwaters.

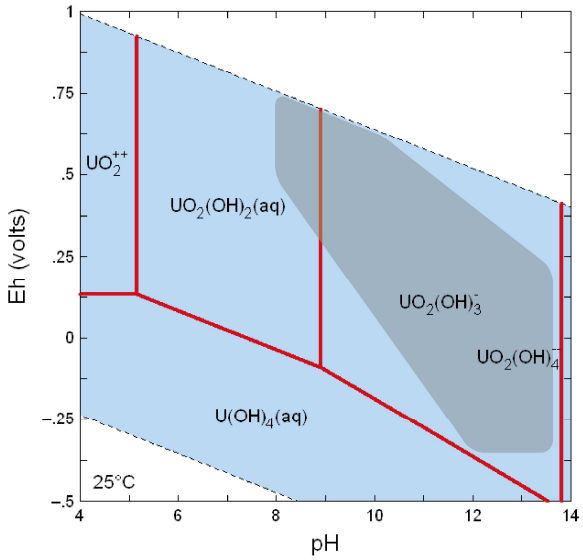

Figure 3-5. Eh-pH Stability Fields for Aqueous Uranium (1×10^{-8} M) in Pure Water at 25 °C (Solids Suppressed) Calculated Using Geochemist's Workbench Version 6.0 With the thermo.com.v8.r6+.dat Database. The Shaded Area Represents the Approximate Range of Expected Conditions as Cement-Based Materials Degrade (Section 2). Addition of Sulfur Does Not Alter the Aqueous Species Fields. The Blue Field Defines Water Stability.

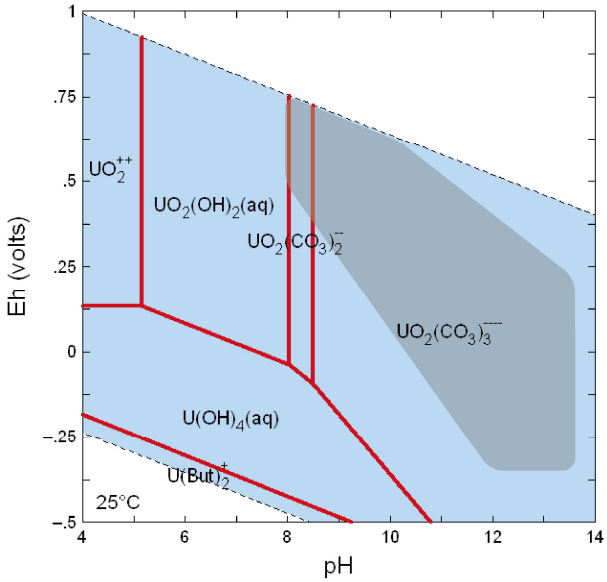

Figure 3-6. Eh-pH Stability Fields for Aqueous Uranium (1×10^{-8} M) in Water at Equilibrium With CO_2 Gas at a Fugacity of $10^{-3.5}$ atm at 25 °C (Solids Suppressed) Calculated Using Geochemist's Workbench Version 6.0 With the thermo.com.v8.r6+.dat Database. The Shaded Area Represents the Approximate Range of Expected Conditions as Cement-Based Materials Degrade (Section 2). The Blue Field Defines Water Stability.

3.3.1 Experimental Data

Numerous studies relevant to uranium solubility in cementitious waters are available in the literature. Ewart, et al. (1992) measured uranium solubilities from oversaturation in CO_2-free conditions in a water equilibrated with a blend of 90 percent BFS and 10 percent OPC; pH was adjusted over a range of 5 to 13. Solubility of U^{IV} was measured at about 2×10^{-7} M over the entire pH range. From pH 5 to 10.5, measured U^{VI} solubility decreased from 10^{-5} to 10^{-7} M and then increased again to 10^{-5} at pH 13. Solids were not identified. Pointeau, et al. (2004) obtained quite similar uranium solubility limits over the pH range 9.3 to 12.2 in waters equilibrated with cement and C-S-H. Maximum uranium concentrations of 3 to 5×10^{-6} M were obtained at the low and high ends of this pH range and, as in Ewart, et al. (1992), a minimum value (2×10^{-7} M) was observed at pH 10.5. Krupka and Serne (1998) claimed that the high-pH data of Ewart, et al. (1992) were consistent with uranophane solubility control.

Moroni and Glasser (1995) performed a systematic experimental study of uranium solubility in the Ca-U-Si system under nonreducing conditions. Measured uranium concentrations at lower uranium loadings at 10 to 13 pH were in the range 1×10^{-9} (or lower) to 1×10^{-7} M; the higher values were associated with solutions compatible with $Ca(OH)_2$. In solutions equilibrated with C-S-H gels, however, concentrations were 1×10^{-8} M and lower. Potential Ca-U mineral phases controlling uranium solubility were analyzed, but uranium phases coexisting with $Ca(OH)_2$ and C-S-H were not definitively identified. One phase was provisionally identified as hydrated $CaUO_4$, but it was not observed in any mixtures containing silica.

Serne, et al. (1996) obtained uranium concentrations of 2×10^{-6} to 2×10^{-8} M in cement pore water in air as controlled pH decreased from 7.5 to 9.0; these were below a detection limit of about 10^{-8} M at higher pH. Identification of a controlling uranium mineral was inconclusive, though an amorphous $CaUO_4$ phase was hypothesized. Greenfield, et al. (1998) reported uranium solubility limits in cement-equilibrated water (pH 12, Eh −500 mV) of $<5 \times 10^{-8}$ M and 2×10^{-7} M. Zhao, et al. (2000), in experiments designed to measure uranium sorption onto hydrothermally altered cement in the absence of CO_2, measured uranium concentrations varying from 3×10^{-6} M at pH 9.2, decreasing to 2×10^{-8} M at pH 10.7, then increasing to 3×10^{-7} M at pH 11.2. Solubility of no one uranium mineral could explain the pH trend, but the concentrations exceeded model curves for $CaUO_4$, uranophane, and haiweeite. Other studies (e.g., Berner, 1992, 1999) have questioned the role of crystalline $CaUO_4$ in controlling uranium concentrations under cementitious conditions, because experimental concentrations typically exceed model $CaUO_4$ solubility. Berner (2002) discussed unpublished uranium solubility studies that yielded a maximum uranium concentration of 2×10^{-6} M at pH 13.3, projected to 5×10^{-7} at pH 12.22.

The picture that emerges from these studies is that, for cementitious systems over the approximate pH range of 9 to 13, uranium concentration is limited to maximum values of 10^{-8} to 10^{-6} M. Lower and higher limits are suggested under certain conditions (e.g., Moroni and Glasser, 1995; Ewart, et al., 1992), but these extremes are not consistently observed. In addition, studies do not consistently point to specific uranium minerals responsible for solubility control.

3.3.2 Models

Uranium solubility models for cementitious systems are common in the literature; only a relatively few examples are discussed here. Model outcomes have varied considerably over the years as thermodynamic databases have evolved. [For example, Berner (2002) chose to not use his model calculations for uranium solubility, which implied little solubility control above an Eh of -300 mV, because of the paucity of uranium phases in his model's database.] Allard and Torstenfelt (1985), noting the low carbonate content of cement pore waters, modeled a U^{IV} solubility limit of 10^{-6} to 10^{-7} M for reducing conditions and a U^{VI} limit under oxidizing conditions of 10^{-6} M. Individual uranium mineral solubilities were calculated by Berner (1992) as pH evolved during cement degradation at Eh −300mV. With the exception of highly insoluble $CaUO_4$, solubility limits changed from around 10^{-4} M to 10^{-7} M as pH dropped from 13 to 10. Brady and Kozak (1995) calculated uranium solubilities of 10^{-8} M and lower for cementitious environments; haiweeite was the controlling phase for oxidizing conditions. Greenfield, et al. (1998) calculated a UO_2(am) solubility of 3×10^{-7} M for a pH 12 water at −500 mV.

Krupka and Serne (1998) modeled schoepite and uranophane solubility for a pH range of 4 to 12.5, with Eh varying from +380 to +200 mV over the pH range. Uranophane constrained uranium to lower concentrations, ranging from 2×10^{-8} to 1×10^{-5} M as pH increased from 8.5 to 12.5. For a model cement pore water at pH 13.4 and Eh −300 mV, Berner (1999) calculated a solubility limit of 5×10^{-7} M, controlled by α-$Na_2U_2O_7$ and with U^{VI} species dominating dissolved uranium. As in many uranium cement models, dissolved carbonate is quite low in this model solution (1.4×10^{-4} M) such that hydroxide uranium species dominate over carbonate species. (See Figure 3-6 for the effect on uranium speciation of carbonate at high pH.)

In an example of the failure of crystalline $CaUO_4$ to match solubility data, Serne, et al. (1996) showed that a model solubility curve for that phase gave concentrations approximately three orders of magnitude lower than experimental results.

Clearly, the success of solubility models depends strongly on the comprehensiveness of the supporting thermodynamic database and on selection of the controlling solid phases. In an attempt to refine uranium predictions, new calculations were performed using the most current database available with the Geochemist's Workbench® software package (thermo.com.v8.r6+.dat). In initial runs, very low uranium solubilities were calculated under many conditions when either $CaUO_4$ (10^{-14} to 10^{-11} M) or haiweeite (10^{-13} to 10^{-8} M) was the limiting mineral. Because these values differ grossly from experimental data and they have not been typically identified in experiments, these solids were suppressed in the models.

Preliminary model results are illustrated in Figure 3-7; water chemical characteristics were discussed in Section 2.5. For some water compositions results for a number of modeled Eh values are shown. Calculated solubility limits vary between 9×10^{-10} and 5×10^{-4} M, with no strong overall variations with pH and Eh. For example, values in the high-pH region (>11) span the entire range, and the highest values are obtained at Eh as low as −200 mV. Solubility limiting minerals are U^{VI} phases $Na_2U_2O_7$, schoepite, and soddyite; U^{IV} phase uraninite; and one instance of mixed-valent $UO_{2.33}$. Inspection of the results shows that the most important factors affecting calculated solubility are aqueous sodium and silica. Carbonate content effects are less important, as demonstrated by the high values obtained at higher Eh for waters 5 and 8, which

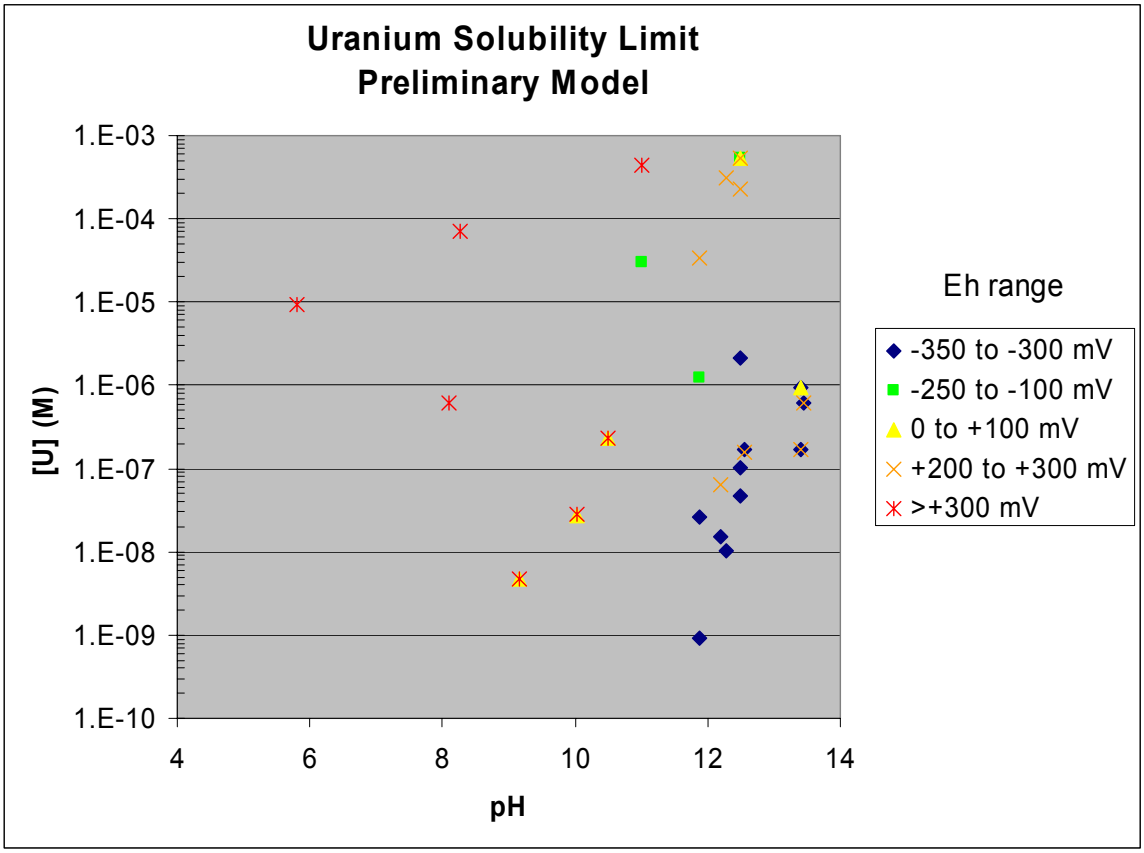

Figure 3-7. Preliminary Results of Uranium Solubility Limit Model Calculated Using Geochemist's Workbench Version 6.0 (SpecE8 and React Modules) With the thermo.com.v8.r6+.dat Thermodynamic Database. Model Values Are for Representative Waters in Table 2-1, With a Range of Selected Eh Values Illustrated for Most Compositions.

do not include carbon species (Table 2-1). The waters yielding the highest calculated uranium concentrations tended to have low or no sodium in their defined water chemistry, such that precipitation of $Na_2U_2O_7$ was avoided. Waters that gave uranium less than 10^{-6} M even at high Eh (Waters 6, 25) were characterized by higher silica contents, such that the uranyl silicate soddyite was favored and the solubility product imposed lower dissolved uranium. These results point to the importance of complete chemical characterization because of the multi-cation nature of many important uranium minerals.

Further analysis, including sensitivity studies, of the preliminary uranium models is warranted. The lower limit of 10^{-8} M bounding most calculated uranium concentrations is, however, similar to the interpretation of the laboratory results (Section 3.3.1). The upper limit to the model results can be refined by considering sodium chemistry more carefully.

3.3.3 Conclusions

While the new modeling results are tentative, literature laboratory data (Section 3.3.1) suggest that uranium concentration limits of as low as 10^{-8} M are potentially viable in evolving cementitious systems when pH is around 12.5 to 11 at lower Eh. At higher and lower pH, such a low limit is more difficult to substantiate, and values exceeding 10^{-6} M are feasible. Clearly, simple assignment of uranium solubility limits to generic conditions must be carried out with great care, taking into particular consideration aqueous sodium, silica, and carbonate contents.

3.4 Neptunium

Like uranium, neptunium aqueous behavior is sensitive to redox conditions and dissolved carbonate. Figure 3-8 shows the Eh-pH dependence of neptunium aqueous speciation in pure water; the two higher Eh species are Np^{V}, while the low-Eh species is Np^{IV}. As seen in Figure 3-9, addition of atmospheric CO_2 gas replaces the high-pH hydroxide species with a variety of carbonate species. These anionic carbonate species may contribute to aqueous neptunium stability at high pH (e.g., Neck, 2006); note, however, that the relative sizes of the Np^{V} and Np^{IV} fields do not change dramatically. (Recall, as discussed in Section 3.3, that atmospheric CO2 may not apply during earlier stages of cement degradation.)

For young and moderately aged cement under reducing conditions (pH 12.5 and 10.5, respectively), Kaplan (2006) recommended neptunium solubility limits of 5×10^{-5} M and 10^{-6} M as conservative and best values, respectively. For aged cements, Kaplan (2006) proposed corresponding limits of 5×10^{-4} M and 10^{-5} M. For oxidizing conditions, the young and moderately aged cement conservative and best values were 5×10^{-7} M and 10^{-8} M, respectively, while the corresponding values for aged cement were 5×10^{-6} M and 10^{-7} M. [Note that, for Kaplan (2006), “aged” conditions assumed a pH of 5.5, corresponding to local groundwaters.]

3.4.1 Experimental Data

Experimental neptunium solubility data specific to cementitious conditions are rare. Ewart, et al. (1986, 1992) reported measured neptunium solubilities for cementitious pore waters in CO_2-free conditions. From pH 9 to 13, Np^{V} concentrations decreased from around 10^{-5} M to 10^{-9} M (Ewart, et al., 1986); the controlling solid was assumed to be $Np^{V}O_2OH$. The authors were unable to model the results unless Np^{V} hydrolysis products, expected to boost solubility at high pH, were neglected. Measured Np^{IV} solubilities clustered around 10^{-8} M with no pH dependence, consistent with a model for $Np^{IV}(OH)_4$ solubility (Ewart, et al., 1992).

Solubility data not focused exclusively on cementitious systems are also relevant. In independent studies of carbonate-containing Yucca Mountain, Nevada, groundwaters, neptunium solubility limits of around 10^{-5} M were measured at pH 8.5 (Nitsche, et al., 1993, 1994; Efurd, et al., 1998). Lierse, et al. (1985) and Neck, et al. (1992) reported solubility measurements of amorphous NpO_2OH in carbonate-free $NaClO_4$ media over the pH range 7 to 13.8. Solubilities decreased from 10^{-4} to 10^{-3} M at pH 8 to a minimum of approximately 10^{-6} M at pH 11.5, then rose to almost 10^{-4} M at pH 13.5. Neck, et al. (1992) pointed to ionic strength effects that depress the concentrations at high ionic strength by half an order of magnitude. The

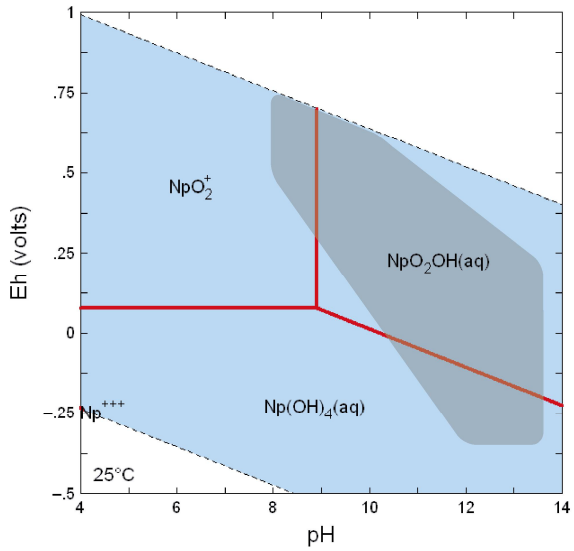

Figure 3-8. Eh-pH Stability Fields for Aqueous Neptunium (1×10^{-8} M) in Pure Water at 25 °C (Solids Suppressed) Calculated Using Geochemist's Workbench Version 6.0 With the thermo.com.v8.r6+.dat Database. The Shaded Area Represents the Approximate Range of Expected Conditions as Cement-Based Materials Degrade (Section 2). Addition of Sulfur Does Not Alter the Aqueous Species Fields. The Blue Field Defines Water Stability.

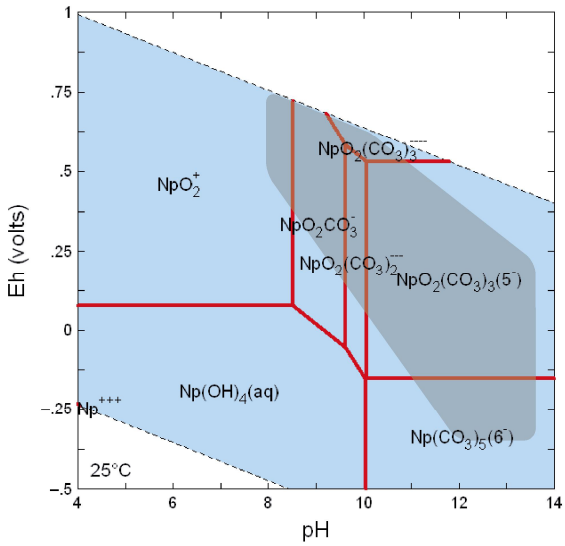

Figure 3-9. Eh-pH Stability Fields for Aqueous Neptunium (1×10^{-8} M) in Water at Equilibrium With CO_2 Gas at a Fugacity of $10^{-3.5}$ atm at 25 °C (Solids Suppressed) Calculated Using Geochemist's Workbench Version 6.0 With the thermo.com.r8.r6+.dat Database. The Shaded Area Represents the Approximate Range of Expected Conditions as Cement-Based Materials Degrade (Section 2). The Blue Field Defines Water Stability.

increase at highest pH was modeled as due to the Np^V hydrolysis product $NpO_2(OH)_2^-$ and contrasts markedly with the decrease Ewart, et al. (1986) measured. Itagaki, et al. (1992) also obtained similar values in $NaClO_4$ media, though they showed an order-of-magnitude dependence on ionic strength (i.e., concentrations at an ionic strength of 0.8 were closer to 10^{-7} M).

3.4.2 Models

Numerous models for neptunium solubility under cementitious conditions have been reported, but the results are strongly dependent on the thermodynamic database employed. In experimental studies discussed in Section 3.4.1, Ewart, et al. (1986) and Neck, et al. (1992) were able to match neptunium concentrations to Np^V thermodynamic models despite strong differences in experimental trends. Matches between models and experiments were possible because Ewart, et al. (1986) chose to neglect all neptunium hydroxyl species, whereas Neck, et al. (1992) were able to match their data using an existing stability constant for the $NpO_2(OH)_2^-$ species. Experimental and laboratory results from the latter study were further supported by Neck (2006). Some published models, like Ewart, et al. (1992) show quite low neptunium solubilities at highest pH. For example, Krupka and Serne (1998) calculated neptunium solubilities from pH 8 and +400 mV to pH 12.5 and Eh +200 mV; the value decreased monotonically from 2×10^{-3} to 9×10^{-6} M, respectively. The model of Krupka and Serne (1998) did include the $NpO_2(OH)_2^-$ species; the authors did not discuss why this species did not cause an increase in neptunium at high pH, but it may be a result of the choice of hydrolysis constants. In all cases cited in this paragraph, the solubility-limiting solid was amorphous NpO_2OH.

For reducing conditions, Berner (1999, 2002) modeled neptunium solubilities of 5×10^{-9} M at pH 12.6 and 13.4, with Eh of −230 and −300 mV, respectively. The solubility, limiting solid was hydrated $Np^{IV}O_2$, and the aqueous species was $Np^{IV}(OH)_4(aq)$. These results generally agree with the Np^{IV} experimental results of Ewart, et al. (1992). Berner (2002) also calculated a concentration of 10^{-3} M at pH 12.6 and Eh +350 mV, but much of this neptunium was attributed to a Np^{VI} species whose existence has not been confirmed. Based on models of concrete pore water, Allard and Torstenfelt (1985) selected a solubility limit of 10^{-7} M for reducing conditions and 10^{-6} M for oxidizing conditions.

New models were constructed in this study for the neptunium solubility limit using the water compositions discussed in Section 2.5. Preliminary results are illustrated in Figure 3-10; for some water compositions, results for a number of modeled Eh values are show. In all runs, tetravalent NpO_2 was calculated to be the solubility-limiting solid. Excluding the pH 5.8 SRS groundwater, modeled solubilities vary over the large range from 3×10^{-18} M to 2×10^{-6} M. While the highest values tend toward the lower pH range, there is no strong correlation with pH. Rather, neptunium solubilities vary strongly with Eh, pointing to the increasing stability of Np^V aqueous species as the system becomes more oxygenated, as well as the fact that the solubility equilibrium under most conditions involves a redox reaction.

These new model results have clearly not reproduced existing laboratory data, particularly considering the very low neptunium concentrations at low Eh (Figure 3-10). Even the very low concentrations of around 10^{-9} M at high pH from Ewart, et al. (1986) far exceed these values. Furthermore, the models are far below the well-constrained experimental values of Lierse, et al. (1985) and Neck, et al. (1992) and do not account for any increase in neptunium concentration

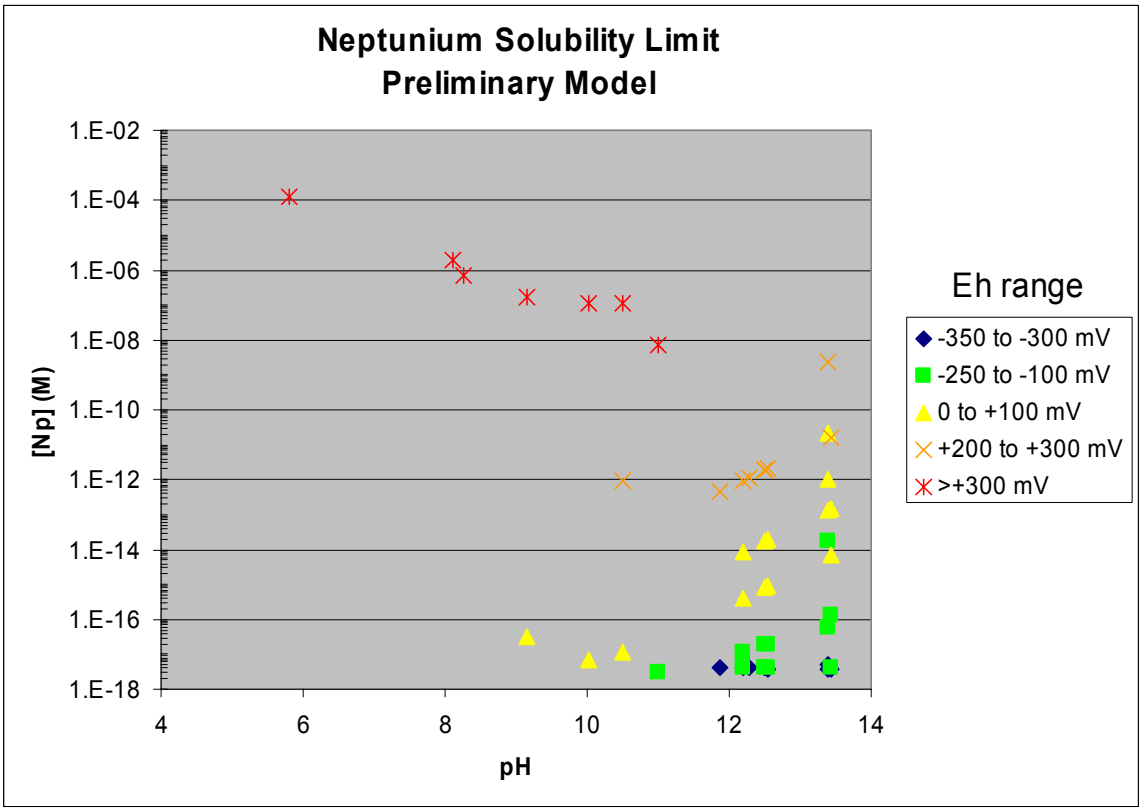

Figure 3-10. Preliminary Results of Neptunium Solubility Limit Model Calculated Using Geochemist's Workbench Version 6.0 (SpecE8 and React Modules) With the thermo.com.v8.r6+.dat Thermodynamic Database. Model Values Are for Representative Waters in Table 2-1, With a Range of Selected Eh Values Illustrated for Most Compositions.

at high pH due to the $NpO_2(OH)_2^-$ species (Neck, et al., 1992; Neck, 2006). The reason for the latter is that the thermodynamic database used for these calculations (thermo.com.v8.r6+.dat) includes only $NpO_2OH(aq)$ and NpO_2OH^+ as Np^V hydrolysis products. (The new models include carbonate, but calculated neptunyl carbonate species are not dominant and have not led to increased stability of dissolved neptunium.) In addition, there is no strong evidence for formation of NpO_2 in published high-pH solubility experiments; in fact, investigators have concluded that Np^VO_2OH and $Np^{IV}(OH)_4$ were the solubility controlling phases. On the other hand, the experiments may have been contaminated by oxygen gas such that Eh was not maintained at very low levels. Clearly, the new model results cannot be directly applied to establishing neptunium solubility limits without consideration of other sources of information. Sensitivity studies of the model results will be conducted in the future, including the possible use of different thermodynamic databases.

3.4.3 Conclusions

Taking a conservative approach that favors higher solubility limits in light of uncertainties, the overall picture from surveying laboratory and model results is that in oxidizing systems,

neptunium solubility varies from approximately 10^{-3} M at pH 8 to 10^{-6} M at pH 11–12. Concentrations may rise again to as high as 10^{-4} M as pH increases to 13. In oxidizing systems, dissolved neptunium will tend to be dominated by $NpO_2OH(aq)$ and NpO_2^+. Under reducing conditions, when Np^{IV} dominates in solution as $Np(OH)_4(aq)$, 10^{-8} M appears to represent a reasonable neptunium solubility limit. The plot in Figure 3-8 is useful for defining these two sets of conditions. These interpretations rely strongly on identifying the solubility limiting solid phase and correctly modeling dissolved Np^V carbonate and hydroxyl species.

3.5 Plutonium

Plutonium geochemistry is complicated by the multiple coexisting oxidation states possible under aqueous conditions. Thermodynamically predicted dominant dissolved species are illustrated in Figures 3-11 and 3-12. In a carbonate-free system (Figure 3-11), the two higher-Eh stability fields overlapped by the polygon represent Pu^V species, while the lower-Eh species is Pu^{IV}. (Hexavalent plutonium species are also present, but are subordinate in concentration.) When atmospheric CO_2 is included (Figure 3-12), the $Pu^VO_2OH(aq)$ field is replaced by an expanded $Pu^{VI}O_2(CO_3)_2^{2-}$ field, such that three plutonium oxidation states are reflected in the dominant species over the range of expected chemistries. Because of the large size of the $Pu(OH)_4(aq)$ stability field even in carbonate-containing waters (Figure 3-12), plutonium solubilities in cementitious waters may, overall, be somewhat less sensitive to carbonate content than uranium and neptunium. Nevertheless, plutonium carbonate species must be considered (e.g., Yamaguchi, et al., 1994).

For young and moderately aged cement under reducing conditions (pH 12.5 and 10.5, respectively), Kaplan (2006) recommended plutonium solubility limits of 5×10^{-9} M and 10^{-10} M as conservative and best values, respectively. For aged cements, Kaplan (2006) proposed corresponding limits of 5×10^{-8} M and 10^{-9} M. For oxidizing conditions, the young and moderately aged cement conservative and best values were 5×10^{-7} M and 10^{-8} M, respectively, while the corresponding values for aged cement were 5×10^{-6} M and 10^{-7} M. [Note that for Kaplan (2006) “aged” conditions assumed a pH of 5.5, corresponding to local groundwaters.]

3.5.1 Experimental Data

Ewart, et al. (1992) measured plutonium solubility as a function of pH in a concrete-equilibrated water under a nitrogen atmosphere (<100 ppm O_2). At pH 8, the plutonium concentration was 10^{-8} M, dropping to 10^{-10} M at pH 9, then was constant out to pH 13 at around 7×10^{-11} M. The authors modeled this trend in concentration versus pH by assuming solubility control by a $Pu(OH)_4$ solid, with the dissolved plutonium in the flat, high-pH portion dominated by the $Pu(OH)_4(aq)$ species. Greenfield, et al. (1998) also measured plutonium in a concrete-equilibrated water under nitrogen atmosphere at pH 12 and Eh around 190 mV; they obtained a solubility of 2×10^{-10} M. These results suggest a solubility limit of 10^{-10} M for plutonium in cement pore water, rising to 10^{-8} M as pH evolves below pH 9.

Studies not focused exclusively on cementitious systems provide further information on plutonium solubility through the pH-Eh region of interest. In a series of experiments on Yucca Mountain region groundwaters adjusted to pH 8.5 (Eh ~270 mV), Nitsche, et al. (1993,

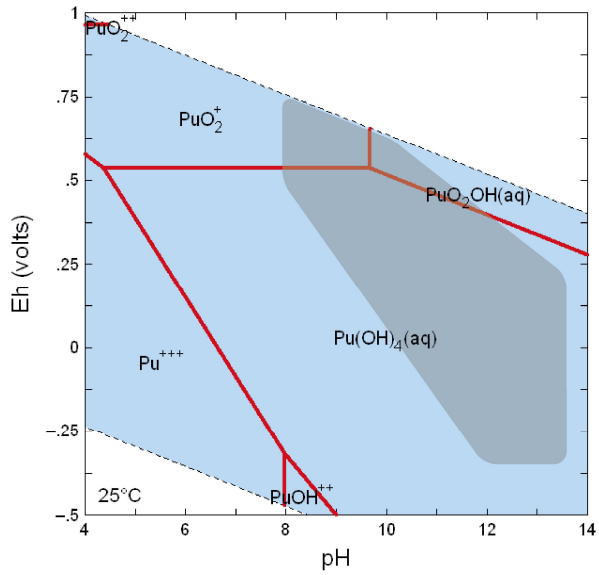

Figure 3-11. Eh-pH Stability Fields for Aqueous Plutonium (1×10^{-8} M) in Pure Water at 25 °C (Solids Suppressed) Calculated Using Geochemist's Workbench Version 6.0 With the thermo.com.v8.r6+.dat Database. The Shaded Area Represents the Approximate Range of Expected Conditions as Cement-Based Materials Degrade (Section 2). Addition of Sulfur Does Not Alter the Aqueous Species Fields. The Blue Field Defines Water Stability.

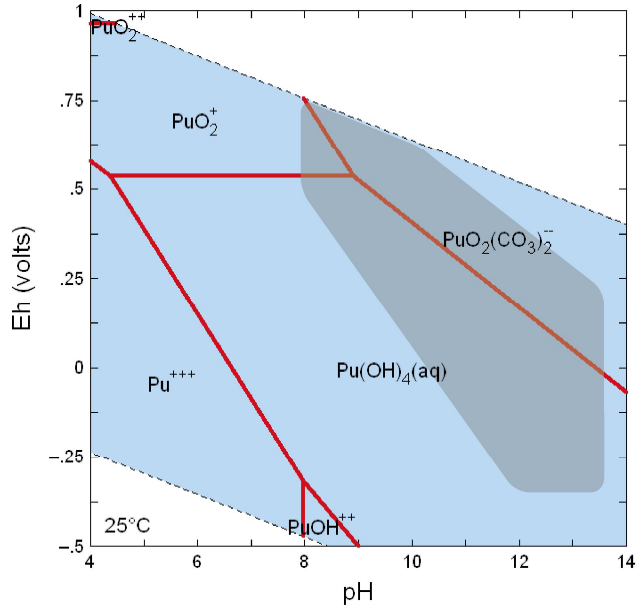

Figure 3-12. Eh-pH Stability Fields for Aqueous Plutonium (1×10^{-8} M) in Water at Equilibrium With CO_2 Gas at a Fugacity of $10^{-3.5}$ atm at 25 °C (Solids Suppressed) Calculated Using Geochemist's Workbench Version 6.0 With the thermo.com.r8.r6+.dat Database. The Shaded Area Represents the Approximate Range of Expected Conditions as Cement-Based Materials Degrade (Section 2). The Blue Field Defines Water Stability

1994) obtained plutonium concentrations of 3×10^{-7} and 1×10^{-6} M, with the solution dominated by Pu^{V}. Another Yucca Mountain study (Efurd, et al., 1998) obtained a value of 10^{-8} M for similar conditions. In interpreting these data and reporting new solids characterization results, Runde, et al. (2002) concluded that plutonium concentrations were too high for equilibrium with a solid phase such as amorphous hydrated PuO_2 [sometimes denoted PuO_2(am, hyd) or $Pu(OH)_4$] and proposed that colloidal Pu^{IV} species were responsible for the excess. Apparently, ultrafiltration at an estimated 4-nm pore size was insufficient to exclude these colloids from the solution.

Neck, et al. (2007) recently summarized data on plutonium solubility in carbonate-free solutions, particularly from their studies and from Rai and co-workers (Rai, et al., 1999). For ultracentrifuged plutonium solutions maintained in an argon atmosphere (<10 ppm O_2), results were quite similar to Ewart, et al. (1992). Total dissolved plutonium was at about 10^{-8} M at pH 8, decreasing to 10^{-10} M at pH 10, then remaining around 10^{-10} M out to pH 13. The system was not particularly reducing, with Eh varying from about +250 mV to −50 mV as pH increased from 8 to 13. Neck, et al. (2007) modeled the results as resulting from solubility of a hydrous, mixed-valent plutonium solid denoted as PuO_{2+x}(am, hyd). Unfiltered solutions, however, showed a consistent colloidal Pu^{IV} concentration of around 10^{-8} M (Log −8.3 ± 1.0) at pH 8 to 13, which the authors attributed to a reproducible equilibrium with dissolved Pu^{V}. Neck, et al. (2007) argue that this colloidal component controls aqueous plutonium over this pH range and cannot be disregarded. It bears repeating that these experiments do not include solution effects of dissolved carbonate, which is nonetheless relatively low in cementitious waters.

3.5.2 Models

A number of researchers have attempted to model plutonium solubility in cement pore waters; only a few examples are presented here. The model of Allard and Torstenfelt (1985), applied to both reducing and oxidizing conditions, used PuO_2 as the controlling phase and suggested a limit of less than 10^{-10} M for cementitious waters with $Pu(OH)_4$(aq) as the dominant aqueous species. The limit would be three to four orders of magnitude higher at highest pH if the $Pu(OH)_5^-$ species were stable, but this species has subsequently been shown to have low stability (e.g., Ewart, et al., 1992). Allard and Torstenfelt (1985) also showed that high aqueous carbonate would raise plutonium concentrations by one to three orders of magnitude at pH above 8. As discussed in Section 3.5.1, models accompanying experiments by Ewart, et al. (1992) and Greenfield, et al. (1998) confirmed a plutonium solubility limit of around 10^{-10} M above pH 9 under conditions that were not strongly reducing. Ewart, et al. (1992) also matched the decrease to 10^{-8} M at pH 8 with their $Pu(OH)_4$ solubility model.

Brady and Kozak (1995) simulated reactions between a pore water and portlandite and C-S-H under both atmospheric and nonoxygenated, non-CO_2 exchanging conditions. The plutonium concentration limit in the former case was 2×10^{-7} M because of $Pu^{VI}O_2(OH)_2$ solubility. For the nonatmospheric case, a model solubility limit of 1×10^{-10} M, similar to other published model results for cementitious conditions, was obtained. For pH 8 to 12.5 (with corresponding Eh varying from 400 to 200 mV), Krupka and Serne (1998) modeled a constant plutonium solubility limit of 1×10^{-10} M, with $Pu^{IV}O_2 \bullet H_20$(am) as the controlling phase. Berner (2002) obtained a somewhat lower limit of 4×10^{-11} M at pH 12.6 and Eh below +300 mV. Clearly, a number of published models, using different codes and databases, have consistently yielded a limit of

around 10^{-10} M for cementitious waters above pH 9. This can be attributed to the apparently low activities of plutonium carbonate species and hydrolysis products more hydrolyzed than $Pu(OH)_4$(aq).

As discussed in Section 3.5.1, the carbonate-free data and models of Neck, et al. (2007) confirm the trend of Ewart, et al. (1992), showing (i) a limit of around 10^{-10} M for waters above pH 9 or 10 and (ii) a rise in solubility to about 10^{-8} M as pH decreases to 8. This plutonium mineral solubility trend for ultrafiltered solubility experiments is illustrated schematically in Figure 3-13. Neck, et al. (2007) propose solubility control by PuO_{2+x}(am, hyd) for this trend, though in detail their curve rises somewhat at highest pH. The approximately 10^{-8} M colloidal Pu^{IV} trend of Neck, et al. (2007) is also shown in Figure 3-13; the authors argue that this is a thermodynamically controlled concentration curve for unfiltered solutions and thus is more applicable to real systems as a concentration limit. This colloidal concentration is consistent with the data of Runde, et al. (2002).

New equilibrium solubility models were constructed for the water chemistries discussed in Section 2.5. Preliminary results are plotted in Figure 3-14; for some water compositions, results for a number of modeled Eh values are shown. Model concentrations are all low, varying from 10^{-17} to 10^{-11} M, and tetravalent PuO_2 was always identified as the solubility limiting solid. As for neptunium, the strongest influence on plutonium solubility was Eh, rather than pH. For all solutions with Eh below +400 mV, solubilities were approximately 10^{-17} M; they rose monotonically with Eh above +400 mV. Dissolved plutonium species were in accord with those shown in Figure 3-11 such that tetravalent Pu(OH)4(aq) dominated most of the field of interest, giving way to pentavalent species at highest Eh. This speciation trend is responsible for the Eh dependence of solubility limit (Figure 3-14. Carbonate species are important only in the two pH 8 waters assumed to be in equilibrium with atmospheric CO_2 (Waters 29 and 30; Table 2-1).

The new model results are not consistent with the reviewed literature information—in particular, the well-established mineral solubility trend illustrated in Figure 3-13 (Although this trend reflects carbonate-poor systems, the relative insignificance of plutonium carbonate species in most model solutions makes this an appropriate comparison.) The key reason for the inconsistency is because amorphous Pu^{IV} or mixed valent oxyhydroxides, rather than crystalline PuO_2, control plutonium solubility (e.g., Neck, et al., 2007) as indicated by experiments and modeling studies. Continued solubility modeling will be conducted that will consider control by different solid phases and different thermodynamic databases.

3.5.3 Conclusions

Considering available information, for pH above 8, the simple trends in Figure 3-13 represent a conservative approach for defining plutonium solubility. The mineral solubility curve appropriately summarizes laboratory results. The constant, apparently equilibrium 10^{-8} M value, however, for colloidal Pu^{IV} polymer over this pH range (Neck, et al., 2007) may more realistically reflect a maximum plutonium concentration. Pending future modeling work that could help establish whether 10^{-8} M is an upper bound to mineral solubility, 10^{-8} M should be considered an appropriate limiting concentration for pH >8.

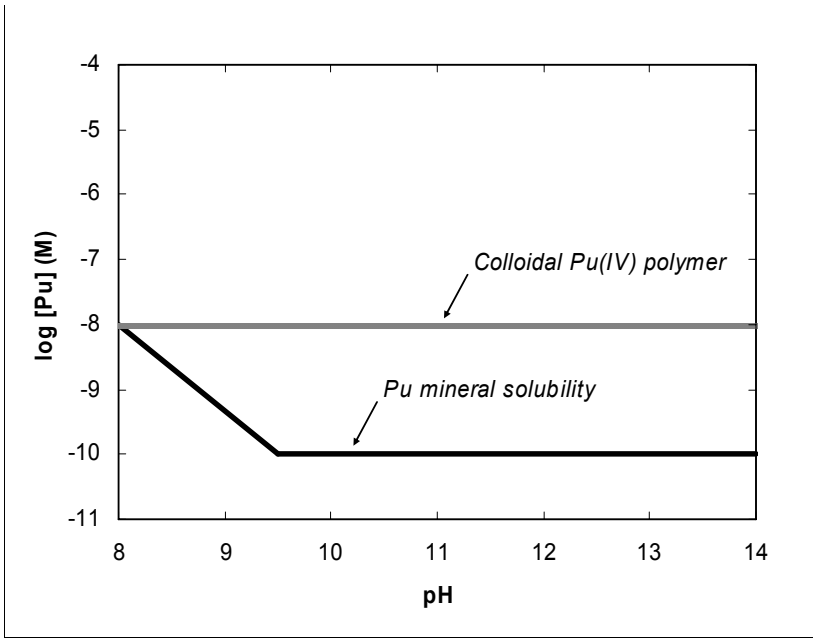

Figure 3-13. Literature Plutonium Concentration Limit Trends for Cement-Based Systems. The Colloidal Pu^{IV} Polymer Value at Approximately 10^{-8} M Is From Neck, et al. (2007). The Pu Mineral Solubility Trend Is From Ewart, et al. (1992); Neck, et al. (2007); and Others (See Text).

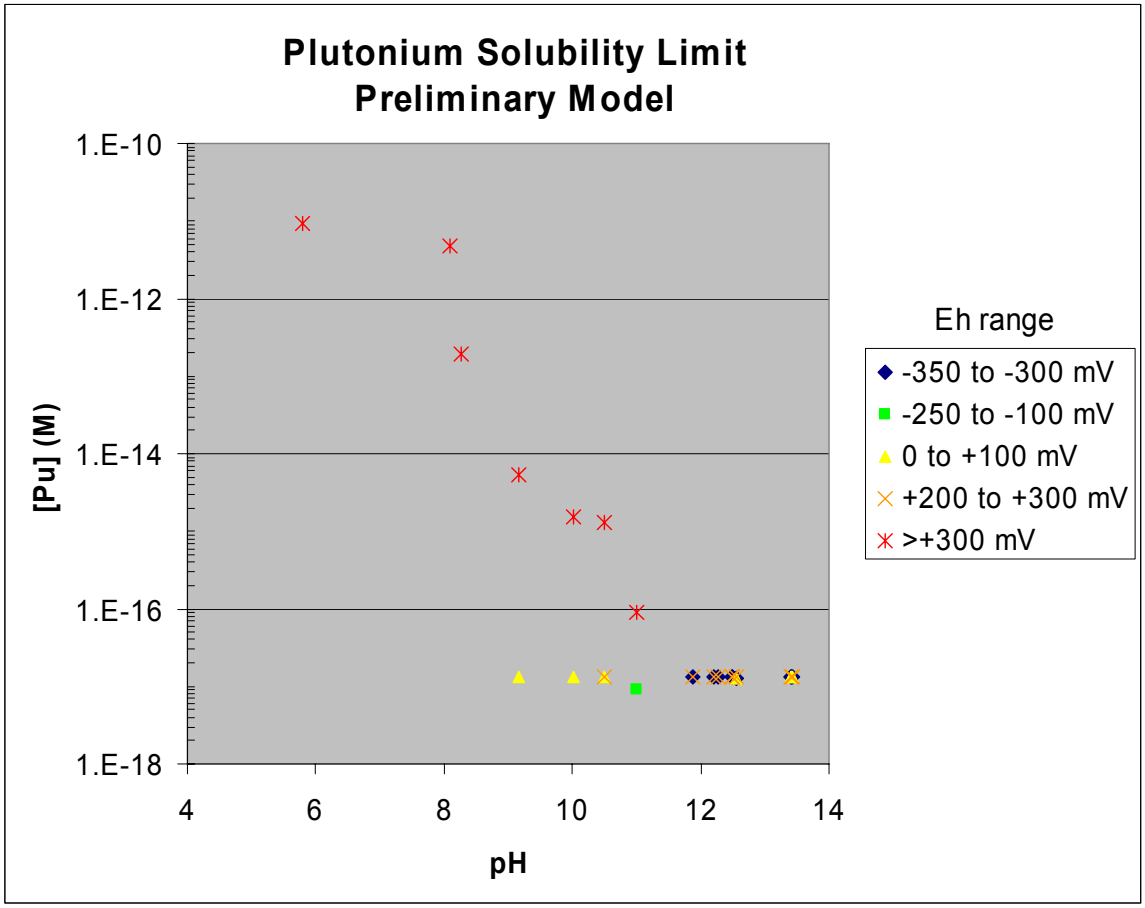

Figure 3-14. Preliminary Results of Plutonium Solubility Limit Model Calculated Using Geochemist's Workbench Version 6.0 (SpecE8 and React Modules) With the thermo.com.v8.r6+.dat Thermodynamic Database. Model Values Are for Representative Waters in Table 2-1, With a Range of Selected Eh Values Illustrated for Most Compositions.

4 SOLUBILITY SUMMARIES FOR OTHER RELEVANT ELEMENTS

This section includes brief summaries of solubility information for the other elements not treated in detail in Section 3.

4.1 Carbon

Carbon-14 may be present in residual waste inventories, and C-14 chemistry is influenced by factors such as carbon dioxide exchange, isotopic exchange, and precipitation. Two recent studies estimate values for solubility of carbon in cementitious waters. Kaplan (2006) recommends a lower solubility at higher pH for both oxidizing and reducing conditions. For young cement at pH 12.5, solubility is approximately 5×10^{-5} M and 5×10^{-6} M for conservative and best values, respectively, and 5×10^{-3} and 5×10^{-4} M for conservative and best values of moderately aged cement at pH 10.5. Krupka, et al. (2004) recommend nearly identical values for both young and moderately aged concrete and appear to be the source of data for Kaplan (2006). Using geochemical reaction path modeling, Brady and Kozak (1995) report carbon solubility at 6×10^{-4} M for oxygenated environments and 2×10^{-3} M for nonoxygenated, no-CO_2 exchange environments. Carbon-14 may be sequestered during carbonation of cement and diluted by ambient nonradioactive carbon in both precipitates and solution. Applying a carbon solubility limit to dissolved C-14 is, therefore, a highly conservative model approach.

4.2 Nickel

Nickel is found in cementitious waters as Ni^{2+}. Experimental solubility of nickel in cementitious waters is reported by Ochs, et al. (1998) for fresh cement at pH 13.2 as 3×10^{-7} M. Solubility decreased for portlandite cement at pH 12.5 to less than 5×10^{-8} M. Kaplan (2006) recommends similar conservative and best nickel solubility values of 5×10^{-6} and 5×10^{-7} M, respectively, for both oxidizing and reducing cements at pH 12.5 and 10.5. Krupka, et al. (2004) recommended 5×10^{-4} M and 5×10^{-7} M as conservative and best values, respectively, for young concrete (pH 12.5), with corresponding values of 5×10^{-4} M and 5×10^{-6} M for moderately aged concrete (pH 10.5).

Berner (1999, 2002) calculated nickel solubilities of 3×10^{-4} to 3×10^{-6} M for pH 13.4 and 3×10^{-7} M for pH 12.6. Krupka and Sterne (1998), however, calculated lower values, decreasing with increasing pH from 6×10^{-6} M at pH 9 to 8×10^{-8} at pH 12.5. Brady and Kozak (1995) modeled nickel solubility at 4×10^{-4} M for oxygenated environments and 8×10^{-13} M for nonoxygenated, no-CO_2 exchange environments.

In summary, most accepted nickel solubility values are close to 10^{-6} M in order of magnitude, but range from as high as 3×10^{-4} M at pH 13.4 (Berner, 1999) to 1×10^{-8} M at pH 11.5 (Krupka and Serne, 1998).

4.3 Strontium

Strontium is divalent in solution. Reported solubility values for strontium vary by several orders of magnitude among various studies. Serne, et al. (1996) report experimental concentrations in

cement leachate as high as 3×10^{-3} M at pH 9 to 13. Berner (2002) recommended strontium solubility of 3×10^{-3} M for pH 12.6 and 1×10^{-6} M for pH 13.4. Ochs, et al. (1998) accepted a literature solubility of 1×10^{-4} M in fresh cementitious water with pH 13.2. Similarly, Brady and Kozak (1995) modeled strontium solubility at 2×10^{-5} M for both oxygenated and nonoxygenated, no-CO_2 exchange environments.

Recommended values by Kaplan (2006) and calculated values by Krupka and Serne (1998) are significantly lower. Both recommend conservative and best values of 5×10^{-6} M and 5×10^{-7} M, respectively, for oxidizing and reducing conditions in pH 12.5 and pH 10.5 waters. Krupka, et al. (2004) suggested conservative and best solubility values of 2×10^{-5} M and 1×10^{-7} M, respectively, for pH 12.5 cementitious waters, increasing to 2×10^{-4} M and 1×10^{-6} M at pH 10.5.

4.4 Niobium

Kaplan (2006) and Berner (2002) concluded that Niobium (V) has no solubility constraints for cementitious pore waters at pH of 5.5–12.5. Talerico, et al. (2004), however, report a decrease in solubility from 2×10^{-5} to 2×10^{-9} M with an increase in pH from 9 to 12. Krupka, et al. (2004) recommended conservative and best solubility values of 5×10^{-4} M and 5×10^{-6} M, respectively, for young near-field concrete (pH 12.5) but 1×10^{-3} M and 5×10^{-4} M for moderately aged concrete water a pH 10.5.

4.5 Tin

Tin is typically present as Sn^{4+} in cementitious waters. Experimental tin solubility in cementitious water was determined to be nontemperature dependent by Ochs, et al. (1998) and in the range of 3×10^{-6} M for fresh cement at pH 13.2 and 4×10^{-8} M for a pH 12.5 portlandite solution. Kaplan (2006) recommends similar values of 5×10^{-7} and 10^{-8} M as conservative and best values, respectively, at oxidizing and reducing conditions at both pH 10.5 and 12.5. Experimentally, Aggarwal, et al. (2001) determined solubility of 3×10^{-8} to 4×10^{-7} M with $CaSn(OH)_6$ as the limiting phase and 9×10^{-2} to 8×10^{-6} M from pore fluid extraction. For near-field water of high pH and young concrete water at 12.5, Krupka, et al. (2004) recommended a slightly higher conservative and best values of 5×10^{-4} and 5×10^{-6} M, increasing to 1×10^{-3} and 5×10^{-4} M at pH 10.5. Berner (1999, 2002) also suggested a best estimate of 10^{-5} M for pH 13.4 and 10^{-7} M at pH 12.6 for cement pore waters.

4.6 Iodine

Iodine, a halogen, is highly soluble and is typically in solution as iodide (iI). Several studies, including those by Kaplan (2006), Krupka, et al. (2004), Aggarwal, et al. (2001), and Berner (2002), conclude that iodine does not have solubility constraints in cementitious waters, regardless of the pH. Specifically studied pH values cover the range 5.5 to 12.5.

4.7 Cesium

Cesium is considered to have no solubility constraints in cementitious pore water, regardless of pH. Kaplan (2006), Krupka, et al. (2004), and Berner (1999) each concluded that cesium is not solubility limited.

4.8 Lead

Lead is among the more soluble of radioelements and is typically present in solution as Pb^{2+}. Ochs, et al. (1998) demonstrated that lead solubility in cementitious waters of fresh cement is 1×10^{-2} M at 22 °C. For leached cement (lower pH), the solubility was lower (4.3×10^{-3} M). Solubility values given by Sanchez, et al. (2002) are considerably lower and show an increase in solubility of lead with increasing pH of leachate water. Solubility increases from 5×10^{-9} M at pH 8 to about 1×10^{-5} M at pH 14 in noncarbonated waters. For carbonated waters, solubility increases from 2×10^{-8} M at pH 8 to 2×10^{-7} M at pH 14.

Kaplan (2006) recommended the same conservative and best solubilities, 5×10^{-7} and 5×10^{-8} M, respectively, for oxidizing cements at pH 12.5 and 10.5 and reducing cements at pH 12.5 and 10.5. These values are taken from those Krupka, et al. (2004) reported for pH 12.5 and 10.5. These results are given as best and conservative values in the context of a near-field environment and on the basis of the presence of lead hydroxy-carbonates, but the supporting information is not traceable from the sources provided in the reference.

4.9 Americium

Americium is typically in solution as a trivalent cation. Ewart, et al. (1992) conducted experiments with americium in cement-equilibrated water with low redox potential that demonstrated a decrease in solubility with increase in pH. Concentrations decreased from 10^{-7} M at pH 8 to 5×10^{-8} M in the range of pH 8.5 to 10.5, and decreased to 10^{-10} M at pH 11 and higher. These experiments were conducted in the presence of calcium carbonate to control the carbonate level in solution and in a nitrogen environment to reduce the atmospheric partial pressure of CO_2 to negligible. They also calculated solubilities predicted by the HARPHRQ model, using the HATCHES database (Cross and Ewart, 1990). Calculated results are similar to experimental results.

Krupka and Serne (1998) used MINTEQ to calculate values for solubility of trivalent americium in cementitious pore waters, which demonstrated a generally decreasing trend in solubility as pH increases (from 4×10^{-9} M at pH 9.5 to 2×10^{-12} M at pH 12.5). Berner (1999, 2002) reported calculation of a higher solubility limit of 2×10^{-9} M for both pH 13.4 and pH 12.6. Similarly, Brady and Kozak (1995) reported a calculated americium solubility of 1×10^{-9} M for oxygenated environments and 4×10^{-9} M for nonoxygenated, no CO_2 exchange environments.

Estimates by Kaplan (2006) of americium solubility vary with pH and type of cement. For young cement at oxidizing conditions and pH close to 12.5, the best estimate solubility is 5×10^{-10} M, similar to the Ewart, et al. (1992) values. Solubility was higher at 5×10^{-7} M for moderately aged oxidizing cement at pH 10.5. The same estimates are given for reducing conditions at the same

pH values and age of cement. Greenfield, et al. (1998) estimate a value of 5×10^{-11} M for experiments using concrete water at pH 12.0 to 12.3, in agreement with a model value.

Other studies show similar results. Krupka, et al. (2004) recommended conservative and best values of 1×10^{-7} and 1×10^{-9} M, respectively, for americium in young concrete at pH 12.5 and 3×10^{-7} and 3×10^{-8} M at the lower pH of 10.5 in moderately aged concrete.

Allard and Torstenfelt (1985) calculated an americium solubility of 10^{-5} to 10^{-6} M in concrete pore waters, assuming stability of the $Am(OH)_4^-$ aqueous species; the solubility would be much lower at 10^{-8} M if only $Am(OH)_3(aq)$ were considered. Counter to the Ewart, et al. (1992) findings, Allard and Torstenfelt (1985) concluded that as pH increases, total americium concentration increases. This difference may be due to the inclusion in the Allard and Torstenfelt (1985) model of the highly soluble americium hydroxyl complex $Am(OH)_4^-$, which has not been substantiated in subsequent studies.

Overall, the highest potential solubility is given by Allard and Torstenfelt (1985) as 10^{-5} to 10^{-6} M at pH 13.5, and the lowest solubility is recommended by Krupka and Serne (1998) as 2×10^{-12} M for pH 12.5. There are several orders of magnitude difference among the various recommendations, and all values at high pH fall in between those values.

4.10 Curium

Curium solubility tends to decrease as pH increases. Kaplan (2006) concluded that data for both oxidizing and reducing conditions of young cement (pH 12.5) suggest a solubility of 5×10^{-10} M as a conservative value and 5×10^{-11} M as a best value. For moderately aged cement at pH 10.5, Kaplan (2006) recommended 5×10^{-7} and 5×10^{-8} M as conservative and best values. Calculated values by Krupka and Serne (1998) are similar, but depend only on the pH of the solution in the calculations. They estimate a 1×10^{-7} and 1×10^{-9} M (conservative/best) for young cement and 3×10^{-7} and 3×10^{-8} M (conservative/best values) for moderately aged cement.

5 CONCLUSIONS

Sections 3.1.3, 3.2.3, 3.3.3, 3.4.3, and 3.5.3 summarize detailed solubility evaluations for selenium, technetium, uranium, neptunium, and plutonium, while Section 4 summarizes the other elements. Important considerations for evaluating solubility limits that are evident in this report are

- The basis for solubility estimations are limited by the investigator's ability to predict geochemical conditions. For example, whether or not selenium and technetium can be considered to be solubility limited at all depends markedly on the ability of the cementitious system to maintain strongly reducing conditions for an extended period of time.

- Solubility models should not be used to recommend solubility values without considering experimental literature. For example, if the Pu^{IV} model of Neck, et al. (2007) is correct, then existing equilibrium modeling codes will predict incorrect plutonium concentration limits.

- The quality and comprehensiveness of the supporting thermodynamic database are critical to modeling and evaluating equilibrium solubility limits.

- Identification of the proper solubility-limiting phase is essential to successful modeling. A model cannot be assumed to predict a real system if nonequilibrium effects are important. This observation points once again to the importance of experimental studies.

- Water chemistry must be completely characterized so that solid phases and aqueous species are accurately predicted.

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