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Evaluations of Mechanisms for Pu Uptake and Retention within Spherical Resorcinol- Formaldehyde Resin Columns

September 2016

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Richland, Washington 99352

Executive Summary

The unexpected uptake and retention of plutonium (Pu) onto columns containing spherical resorcinol-formaldehyde (sRF) resin during ion exchange testing of cesium (Cs) removal from alkaline tank waste was observed in experiments at both the Pacific Northwest National Laboratory (PNNL) and the Savannah River National Laboratory (SRNL). These observations have raised concern regarding the criticality safety of the Cs removal unit operation within the low-activity waste pretreatment system (LAWPS). Accordingly, studies have been initiated at Washington River Protection Solutions (WRPS), who manages the operations of the Hanford Site tank farms, including the LAWPS, PNNL, and elsewhere to investigate these findings.

As part of these efforts, PNNL has prepared the present report to summarize the laboratory testing observations, evaluate these phenomena in light of published and unpublished technical information, and outline future laboratory testing, as deemed appropriate based on the literature studies, with the goal to elucidate the mechanisms for the observed Pu uptake and retention.

This report is structured with the following elements:

- Summary of the PNNL and SRNL Cs ion exchange test observations
- Examination of the technical literature to identify other instances of Pu uptake or precipitation in ion exchange processing from alkaline media
- Outline of the bases for criticality concerns arising from the Pu uptake
- Overview of Pu chemistry in alkaline media and comparison of the behavior with the behaviors of other metals, particularly Fe, a potent neutron absorber
- Summary of Pu solution concentration in SRS (Savannah River Site) and Hanford Site tank wastes as functions of tank solution composition
- Examination and consideration of potential mechanisms for Pu uptake and retention as observed in the sRF testing
- Outline of a staged incremental experimental approach to elucidate the underlying reasons for the observed Pu uptake and retention in the PNNL and SRNL tests and examine potential eluents to enhance Pu stripping from the sRF.

Acronyms and Abbreviations

BET	Brunauer-Emmitt-Teller
CSER	criticality safety evaluation report
CUF	crossflow ultrafiltration/ultrafilter
CV	column volumes
DBP	dibutyl phosphate
DF	decontamination factor
DPM	disintegrations per minute
EDS	energy dispersive spectroscopy
GGRF	ground gel resorcinol-formaldehyde
ICD	Interface Control Document
IDMS	Integrated Data Management System
iQID	ionizing-radiation Quantum Imaging Detector
IX	ion exchange
LANL	Los Alamos National Laboratory
LAWPS	low-activity waste pretreatment system
NAS	sodium aluminosilicate
PFP	Plutonium Finishing Plant
PNNL	Pacific Northwest National Laboratory
PRF	Plutonium Reclamation Facility
REDOX	Reduction Oxidation (reprocessing plant)
RF	resorcinol-formaldehyde
SEM	scanning electron microscopy
sRF	spherical resorcinol-formaldehyde
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TBP	tributyl phosphate
TIC	total inorganic carbon
TOC	total organic carbon
TWINS	Tank Waste Information Network System
WRPS	Washington River Protection Solutions
WTP	Waste Treatment and Immobilization Plant
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction

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1.0 Introduction and Overview of Pu Uptake Observations in Testing of sRF and RF Resin

Both PNNL (Fiskum et al. 2009) and SRNL (Nash and Duignan 2010) have undertaken comprehensive ion-exchange column tests to determine the performance of spherical resorcinol-formaldehyde (sRF) resin in removing radioactive Cs (largely present as ^{137}Cs) from actual alkaline waste solutions from the Hanford Site and from the Savannah River Site (SRS), respectively. The sRF beads, in the hydrogen ion (H^+) form shown in Figure 1, are highly uniform in shape and diameter. The bead diameter is $\sim 400\ \mu\text{m}$ in the H^+ form; when in the sodium (Na^+) form used in the Cs ion-exchange removal step, the beads swell to $\sim 450\ \mu\text{m}$ diameter (Duignan and Nash 2009a).

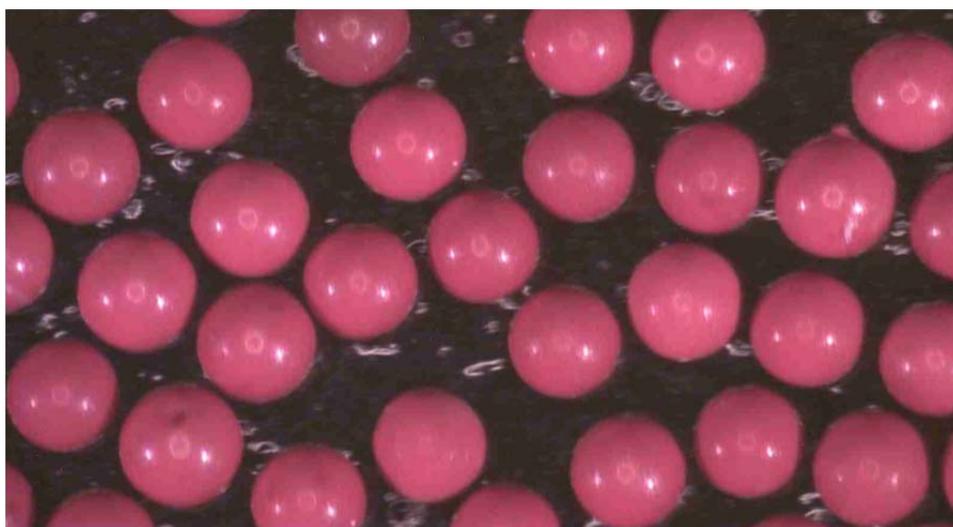


Figure 1. Image of sRF Resin in H^+ Form (Duignan and Nash 2009a)

Both sets of tests also examined elution of the absorbed Cs using nitric acid (HNO_3) solution. In both sets of testing, an appreciable fraction of the Pu was retained on the resin during loading with some of that Pu still remaining with the resin even after the elution step.

To further investigate these observations of Pu uptake onto sRF, prior studies of Cs uptake on sRF and on granular resorcinol-formaldehyde resin from Hanford-origin tank-waste solutions also were surveyed. The survey found three additional studies that provide information on Pu uptake and elution from sRF and from ground gel resorcinol-formaldehyde (GGRF) resin (Fiskum et al. (2006a); Fiskum et al. (2006c), and Hassan and Adu-Wusu (2003), respectively). Each of these three tests used actual Hanford tank-waste solutions. Other studies of Cs uptake and elution from simulated tank-waste solutions onto sRF are available, but none of these studies included Pu in the simulant make-up.

This section of the report examines the results from these five sets of studies.

1.1 Compositions of the Actual Waste Solutions Used in Testing

Table 1 summarizes the compositions of the solutions loaded to the sRF columns in the PNNL and SRNL tests and the single RF test performed at the Westinghouse Savannah River Research Center. The nominal 5-M total sodium (Na^+) concentration for feed to the ion exchange system was observed in all five tests. Hydroxide (OH^-) concentrations in the five actual-waste test solutions ranged from 0.81 to 2.76 M. The most prevalent other anion was nitrate, NO_3^- , at 0.71 to 3.53 M. Nitrite (NO_2^-) was present at 0.17 to 0.88 M. Carbonate (CO_3^{2-}) was reported directly for only two of the feed solutions, at 0.24 and 1.18 M, was estimated from other analyses of solutions intermediate values for two other tank wastes, and was not reported for the SRS tank-waste tests (Nash and Duignan 2010). Aluminate ($\text{Al}(\text{OH})_4^-$) concentrations in the five tests ranged from 0.09 to 0.46 M. Uranium (U) concentrations ranged from 5.21×10^{-6} to 1.79×10^{-4} M, a factor of 34, and thus more widely than the Pu concentrations which ranged only a factor of seven, from 4.67×10^{-9} to 3.29×10^{-8} M. The Pu concentrations were found not to correlate with concentrations of nitrate, nitrite, carbonate, aluminate, and uranium but generally decreased with increasing hydroxide concentration. Such a correlation may only be incidental. The U concentrations did not correlate with any of the anion concentrations.

Table 1. Compositions of Actual Tank-Waste Solutions Used in sRF and RF Testing

Component	Concentration, M, in Filtered Waste Feed Solutions for RF and sRF Resins				
	sRF	sRF	RF	sRF	sRF
	Comp. REDOX Sludge & Saltcake Sol'n.	SRS Tanks 25F and 41H	AW-101	AP-101 Diluted	AN-102
Na ⁺	4.50	6.05	4.94	5.13	4.94
K ⁺	0.01	0.01	0.51	0.74	0.03
OH ⁻	2.76	0.81	2.09	1.98	1.07
CO ₃ ²⁻	0.24	Not reported	1.18	0.54 (est.)	0.56 (est.)
NO ₃ ⁻	0.71	3.53	1.44	1.82	1.64
NO ₂ ⁻	0.28	0.17	0.73	0.82	0.88
Al(OH) ₄ ⁻	0.27	0.32	0.46	0.25	0.09
PO ₄ ³⁻	0.03	0.01	0.00	Not reported	0.02
SO ₄ ²⁻	0.02	0.12	0.00	0.03	0.07
Cl ⁻	0.03	Not reported	0.07	0.04	0.05
Total Pu	4.67×10 ⁻⁹	1.94×10 ⁻⁸	1.35×10 ⁻⁸	5.86×10 ⁻⁹	3.29×10 ⁻⁸
U	1.53×10 ⁻⁵	1.93×10 ⁻⁵	5.21×10 ⁻⁶	1.79×10 ⁻⁴	3.39×10 ⁻⁵
Reference	(Fiskum et al. 2009) ^a	(Nash and Duignan 2010) ^b	(Hassan and Adu-Wusu 2003) ^c	(Fiskum et al. 2006a) ^d	(Fiskum et al. 2006c) ^e

a – From Tables 5.10 and 5.11 of Fiskum et al. (2009).
Pu concentrations for tests with Hanford wastes are based on ^{239,240}Pu analyses and the Pu isotopic composition of 0.021 wt% ²³⁸Pu, 93.9 wt% ²³⁹Pu, 5.86 wt% ²⁴⁰Pu, 0.163 wt% ²⁴¹Pu, and 0.044 wt% ²⁴²Pu derived by decay-correction to 1 July 2008 from best-basis tank-waste inventories found in Table ES-2 of Kupfer et al. (1999).

b – From Tables 1 and 8 and the associated text of Nash and Duignan (2010).
For SRS test solutions, ²³⁸Pu, assuming 83 mass% ²³⁸Pu in production lots (Sprinkle 1991), represents about 17 mass% of the total Pu. The isotopic composition of the balance of the Pu, from weapons-grade Pu production, is assumed to be the same as that of Hanford tanks, as stated above in footnote a. The total Pu concentrations in the SRS test solutions are summed based on separate ²³⁸Pu and ^{239,240}Pu analyses and isotopic compositions.

c – From Table 3-3 of Hassan and Adu-Wusu (2003). For Pu concentration calculations, see footnote a.

d – From Table 3.3 of Fiskum et al. (2006a). Carbonate from Table 3.5 of Fiskum et al. (2000). For Pu concentration calculations, see footnote a.

e – From Table 3.3 of Fiskum et al. (2006c). Carbonate estimated from Table 4.5 of Burgeson et al. (2003) and proportioned to Na⁺ concentrations. For Pu concentration calculations, see footnote a.

1.2 Description of Testing and Pu Uptake Results

1.2.1 Fiskum et al. (2009)

Fiskum and colleagues' (2009) performed tests at Hanford to investigate, on a bench-scale, the pretreatment processing of actual tank-waste materials through the entire nominal Hanford Tank Waste Treatment and Immobilization Plant (WTP) pretreatment flowsheet. These steps included

- caustic leaching to dissolve Al phases from sludge solids,

- crossflow ultrafiltration (CUF),
- washing of solids retained on the CUF,
- oxidative leaching of the sludge residues using sodium permanganate to dissolve chromium solids,
- further solids filtration and washing to remove the manganese dioxide produced in the permanganate treatment,
- ion exchange processing for Cs removal from the solutions (using sRF Microbeads lot number 6C-360-745),
- evaporation of the Cs-stripped solutions for volume reduction, and
- combining the evaporated/concentrated solution product with dissolved saltcake (Fiskum et al. 2009).

The testing used a blend of REDOX sludge (from tanks 241-S-101, -107, and -110 and 241-SX-103) and S-type saltcake (from tanks 241-S-106 and -111, 241-SX-102, -105, and -106, 241-SY-103, and 241-U-103 and -108). The sludge, which contained significant amounts of the Al-bearing solids boehmite, AlOOH, underwent leaching with heated NaOH solution to dissolve the Al solids and form soluble sodium aluminate, NaAl(OH)₄. An earlier report (Fiskum et al. 2008) provides further detail on the preparation and mass bases of the actual sludge and salt cake test material.

The Hanford tests found that 4.4% of the dissolved Pu was retained on the sRF column during loading (Section 5.4.2 of Fiskum et al. (2009)), 92.8% in the ion-exchange column effluent, 1.5% in the feed displacement, and 0.18% of the initially dissolved Pu remaining on the column even after the prescribed elution using 0.5 M nitric acid, HNO₃ (Section 7.2 of Fiskum et al. (2009)). The overall Pu material balance was excellent, 98.8%. Though 4.4% of the dissolved Pu stayed with the column, 99.8% of the total Pu was present in the solid phases, even after oxidative leaching using permanganate, with only 0.2% found in the solution phase. The researchers judged the Pu fed to the sRF column, derived from the REDOX sludge and S-type saltcake digestates, to be in solution because it had passed the CUF's 0.1- μ m pores.

1.2.2 Nash & Duignan (2010)

Scientists from SRNL tested the performance of sRF (Microbeads Lot 5E-370/641) in removing Cs from alkaline radioactive waste solution from nuclear fuels reprocessing at SRS. In the SRNL tests, the actual waste solution was derived from dissolved saltcake from SRS tanks 25F and 41H that had been filtered at 0.2 μ m (Nash and Duignan 2010; Duignan and Nash 2009a; Nash and Duignan 2009). In the SRNL tests, 38% of the dissolved Pu was retained on the sRF resin column and 9% of the original input Pu remained on the column even after elution by 0.5 M HNO₃. No measurements of the column effluent were made, preventing any estimate of material balance. The Pu distributions were based on ²³⁸Pu because of its higher radiometric activity in the dissolved salt cake. However, the chemical concentration of Pu was 81 mole% ^{239,240}Pu and associated isotopes from the weapons-grade Pu stream.

While it was the observation of Pu retention on sRF resin in the two tests reported by Fiskum et al. (2009) and Nash and Duignan (2010) and their related reports that instigated the present interest in the behavior of Pu on sRF, earlier studies of sRF and of its predecessor RF resin, GGRF resin, also indicated Pu uptake by processing of actual wastes.

1.2.3 Hassan & Adu-Wusu (2003)

Hassan and Adu-Wusu (2003) investigated the uptake of Cs and Pu onto GGRF using 0.1- μm (Mott sintered metal) filtered Hanford waste solution from tank 241-AW-101. Pu material balances, based on $^{239,240}\text{Pu}$, were poor in these tests; and the material balances based on ^{238}Pu likewise were poor, but with lower confidence due to lower radiolytic concentrations. However, the data showed $\sim 42\%$ retention of Pu in the resin after loading constituted of $\sim 32\%$ found in the 0.5 M HNO_3 eluate and $\sim 9\%$ remaining in the resin after elution (within rounding error). These values are similar to the 38% of dissolved Pu retained on the sRF resin column after the loading step and 10% of the original input Pu remaining on the sRF column after 0.5 M HNO_3 elution for SRS tank waste (Nash and Duignan 2010).

1.2.4 Fiskum et al. (2006a)

In 2006, PNNL researchers Fiskum and colleagues (2006a; 2006c) conducted two sets of studies of sRF performance in Cs ion exchange processing of actual waste solutions from Hanford tanks AP-101 and AN-102, respectively. Both studies also included analyses of Pu disposition, and both studies used the same resin without replacement and without analysis between runs (Fiskum et al. 2006a; Fiskum et al. 2006c). The sRF resin used was Microbeads Lot 5E-370/641, the same lot as used by Nash and Duignan (2010) but different from that used by Fiskum et al. (2009). The resin at the completion of the second study (Fiskum et al. 2006c) was analyzed for residual Pu (and other analyte) concentrations in subsequent testing.

The first test used 0.45- μm filtered and diluted waste solution from Hanford tank AP-101. This solution passed through an 11-mL bed volume of Na^+ -form sRF resin (Fiskum et al. 2006a). Both the effluent from loading the resin and the eluate arising from elution using 0.5 M HNO_3 were analyzed for Pu concentration ($^{239,240}\text{Pu}$ concentrations were used in the present evaluations because of the lower analytical certainty). The effluent analysis showed $\sim 114.9\%$ of the feed Pu quantity (i.e., the amount was over-recovered). The 0.5-M HNO_3 eluate (from the lead column only) contained $\sim 8.9\%$ of the input Pu. The residual Pu found in the resin following the subsequent test using tank AN-102 waste indicates no more than 0.5% of the total (AP-101 and subsequent AN-102) Pu remained, but it could have been as high as 4.5% of the input Pu from AP-101 had there been no contribution from the subsequent AN-102 test. Although the material balance was less than optimal, the discovery of 8.9% of the Pu in the eluate indicates significant retention of Pu occurred on loading the sRF column with AP-101 solution. Because the resin was analyzed only after this test, the amount of Pu remaining on the sRF resin after elution using 0.5 M HNO_3 is not known with certainty. Based on the eluate and range of sRF analyses, Pu retention on the sRF in the loading cycle was $(8.9+0.5=) 9.4$ to $(8.9+4.5=) 13.4\%$.

1.2.5 Fiskum et al. (2006b)

The second PNNL study of 2006 was similar to the first, but used the eluted sRF resin (Microbeads Lot 5E-370/641) remaining from the AP-101 test rather than fresh resin. Again, the amount of Pu remaining

on the sRF from the prior AP-101 test is unknown. In this second study, (Fiskum et al. 2006c) passed 0.45- μm filtered waste solution from Hanford tank AN-102 through lead and lag 11-mL bed-volume columns of reconstituted Na^+ -form sRF resin, eluting with 0.5 M HNO_3 . As in the prior test, the effluent from loading the resin and the 0.5 M HNO_3 eluate were analyzed. The resin had already processed the AP-101 solution from the prior test and then was used to process the AN-102 solution from the present test. The effluent contained 86.3% of the input Pu and the eluate (from the lead column only) contained 0.9% of the input Pu. The sRF resin held 0.48% of the total Pu processed from both the AP-101 and AN-102 tests and 0.54% of the Pu from the AN-102 test alone (i.e., presuming the elution in the prior AP-101 test had been complete). The presence of 86.3% of the Pu in the effluent suggests some Pu retention on the sRF occurred but the eluate only contained 0.9% of the input Pu and the eluted resin only \sim 0.5% of the input Pu. Therefore, Pu retention on the sRF resin in the loading cycle was likely \sim 1.4%. Of the five waste streams tested, only AN-102 waste contains organic complexing agents. These may have diminished Pu uptake by the resin as compared with uptakes observed for the four other sRF and RF tests. In prior tests with simulated complexed alkaline waste, Pu uptake onto various ion-exchange media and solid sorbents increased following hydrothermal treatment designed to destroy those complexants (Marsh et al. 1995).

Table 2 compares the Pu dispositions in the sRF and RF ion-exchange testing with all five actual-waste tests. The analyses of the individual solution and stripped resin fractions were incomplete for many of these ion-exchange tests leading, in some cases, to the relatively poor or unknown Pu material balances also given in Table 2. Nevertheless, the data are sufficient to show that from about 1.4 to 38% of the input dissolved Pu was retained on the sRF resin on loading, based on the sum of Pu percentages found in the eluate and stripped resin fractions.

Table 2. Pu Distributions in sRF and RF Column Testing

Fraction	Pu Distribution, %, in RF and sRF Resin Column Testing				
	sRF	sRF	RF	sRF	sRF
	Comp. REDOX Sludge & Saltcake Sol'n.	SRS Tanks 25F and 41H	AW-101	AP-101 Diluted	AN-102
Feed	100.0	100.0	100.0	100.0	100.0
Effluent	92.8	Not reported	6.0	114.9	86.3
Feed Disp.	1.5	Not reported	Not reported	Not reported	Not reported
Eluate	4.2	27.0	32.2	8.9	0.9
Resin	0.18	9.1	9.4	0.5-4.5	~0.5
Mat'l. Bal. ^f	98.8	--	47.6	124.3-128.2	88.2
Reference	(Fiskum et al. 2009) ^a	(Duignan and Nash 2009b) ^b	(Hassan and Adu-Wusu 2003) ^c	(Fiskum et al. 2006a) ^d	(Fiskum et al. 2006c) ^e

a – For ^{239,240}Pu Derived from Table 5.11 of Fiskum et al. (2009)
b – For ²³⁸Pu Derived from Tables II, VI, and VIII of Nash and Duignan (2009) and the associated text of (Nash and Duignan 2010)
c – For ^{239,240}Pu Derived from Tables 3-3, 4-6, and 4-8 and text of Hassan and Adu-Wusu (2003)
d – For ^{239,240}Pu Derived from Tables 2.3, 3.3, and 3.5 and text of (Fiskum et al. 2006a) and Table 3.5 of Fiskum et al. (2006b) (resin)
e – For ^{239,240}Pu Derived from Tables 3.3 and 3.5 and text of Fiskum et al. (2006c) and Table 3.5 of Fiskum et al. (2006b) (resin)
f – Mat'l. Bal. is Material Balance = Effluent + Feed Disp.(laced) + Eluate + (stripped) Resin and should =100

1.3 Uranium Uptake Results

The five tests evaluated U dispositions in a fashion similar to those for Pu to help determine whether U and Pu behave similarly. For the blend of digested REDOX sludge and S-type saltcake (Fiskum et al. 2009), 95.1% of the U passed through the sRF column in the effluent. About 2.3% was retained on the resin after loading and feed displacement, as determined by elution using 0.5 M HNO₃ and the remainder of only ~0.008% on the stripped resin.

Very little of the dissolved U reported to the sRF resin in the tests using dissolved SRS salt cake (Duignan and Nash 2009b). Less than 0.021% of the U was found in the eluate from 0.5 M HNO₃ treatment; <0.002% of the U remained in the stripped resin. Thus, no more than ~0.03% of the input U was retained on the sRF during the loading step. Because no U analysis was reported for the effluent from loading, no confirmation is available of the low U retention on the resin.

The tests of GGRF resin performance conducted for waste from Hanford tank AW-101 reported no analyses of U disposition (Hassan and Adu-Wusu 2003).

In the tests of Cs disposition using diluted waste solution from tank AP-101 (Fiskum et al. 2006a), 94.4% of the U passed through the sRF column in the effluent, with about 2.5% removed from the loaded resin

in the 0.5 M HNO₃ eluate and 1.0-1.3% remaining in the resin after elution. Therefore, nearly 4% of the input U was retained on the sRF resin in the Cs loading step for the AP-101 waste solution.

The subsequent tests of Cs disposition using waste solution from tank AN-102 (Fiskum et al. 2006c) used the stripped sRF resin left from the AP-101 tests (Fiskum et al. 2006a). About 95% of the dissolved U passed through the sRF resin column in the effluent, with 4.3% of the input U reporting to the 0.5-M HNO₃ eluate from the loaded resin and 1.0-4.7% remaining on the resin after the elution. The reasons for the resin analysis ranges in the tests for the AP-101 and AN-102 waste solutions is that the same resin was used for both tests and that no analyses of the resin were performed between the runs to apportion the U. Thus, ~5 to 9% of the input U remained on the sRF resin during the Cs loading step for the AN-102 waste.

Table 3 summarizes the U distribution results for the five column tests. Where analyses of the separate fractions are complete (i.e., (Fiskum et al. 2006a; Fiskum et al. 2009; Fiskum et al. 2006c), U material balances are excellent. The amounts of U retained on the resin during the Cs loading step range from <0.023% (for the dissolved SRS salt cake) to 2.2%, and as much as ~9% for the Hanford tank-waste solutions. The extents of U and Pu retention appear to be inversely correlated. Thus, the lowest U retention is found for the dissolved SRS saltcake, while ~38% of the Pu was retained. Conversely, U retention for the AN-102 waste solution was 5-9%, the greatest observed of the five tests, but the Pu retention was the lowest observed, ~1.4% (Fiskum et al. 2006c).

Table 3. Uranium Distributions in sRF and RF Column Testing

Fraction	Uranium Distribution, %, in RF and sRF Resin Column Testing				
	sRF	sRF	RF	sRF	sRF
	Comp. REDOX Sludge & Saltcake Sol'n.	SRS Tanks 25F and 41H	AW-101	AP-101 Diluted	AN-102
Feed	100.0	100.0	100.0	100.0	100.0
Effluent	95.1	Not reported	Not reported	94.4	95.0
Feed Disp.	1.6	Not reported	Not reported	Not reported	Not reported
Eluate	2.2	<0.021	Not reported	2.5	4.3
Resin	0.008	<0.002	Not reported	1.0-1.3	1.0-4.7
Mat'l. Bal. ^f	98.9	--	--	97.9-98.2	102.4-106.1
Reference	(Fiskum et al. 2009) ^a	(Nash and Duignan 2010) ^b	(Hassan and Adu-Wusu 2003) ^c	(Fiskum et al. 2006a) ^d	(Fiskum et al. 2006c) ^e

a – Derived from Table 5.10 of Fiskum et al. 2009 Fiskum et al. (2009)
b – Derived from Table 8 and associated text of Nash and Duignan (2010)
c – No U distribution data reported by Hassan and Adu-Wusu (2003)
d – Derived from Tables 2.3, 3.3, and 3.4 and text of Fiskum et al. (2006a) and Table 3.4 of Fiskum et al. (2006b)
e – Derived from Tables 3.3 and 3.4 and text of Fiskum et al. (2006c) and Table 3.4 of Fiskum et al. (2006b)
f – Mat'l. Bal. is Material Balance = Effluent + Feed Disp.(laced) + Eluate + (stripped) Resin and should =100

1.4 Summary of Pu Uptake Observations in Testing of sRF and RF Resin

The retention of dissolved Pu onto the sRF and RF resin columns in the five evaluated test series ranged from about 2% to 38% of the input quantities; the amount of Pu remaining on the resin after elution using 0.5 M HNO₃ ranged from 0.2 to 9.4% of the input.

The retention of Pu onto the cation-exchanging RF resin is unexpected because, as we will discuss, the dissolved Pu is expected to be anionic and thus should be electrostatically repelled by the resin to pass quantitatively through the column. The U also is expected to be anionic in the highly alkaline tank-waste solutions and thus also should not be retained on the resin, but it, too, is retained in some tests (near 0 to as much as 9% of the input quantities, before elution), though not to as great an extent as Pu.

The Pu retention becomes a nuclear criticality concern because of the potential for excessive fissile Pu accumulation in the large-diameter column geometry required for processing the enormous volumes of Hanford tank-waste solution and digested saltcake and sludge solution for Cs removal in LAWPS pretreatment. A later section of this report explores the criticality concerns. But before criticality concerns are addressed, we will examine other instances of Pu uptake from alkaline solution onto organic ion-exchange resins.

2.0 Other Experience of Pu Uptake from Alkaline Media onto Organic Ion-Exchange Resins

Other experience exists in the decontamination of radioactive alkaline waste solutions using ion-exchange materials or other sorbents in column-type processes. While most of these studies and plant processes were designed to remove Cs, they also obtained or produced data from which incidental information on Pu removal can be inferred. There are also more general surveys of radionuclide uptake from alkaline solution onto organic ion-exchange media or other sorbents. The findings from these various studies comprise the following section of the present report.

2.1 Superlig-644

Past PNNL studies are useful for comparing the behavior of Pu in tests to capture Cs from alkaline tank-waste solutions in sRF with that observed in prior PNNL tests using Superlig-644 (SL-644) resin as a Cs-separation medium (Fiskum et al. 2004b, a). Superlig-644 is a proprietary resin that functions to remove Cs from solution by (“crown ether”) chelation rather than by ion exchange as sRF resin does.

In the prior tests with SL-644, researchers found that most of the dissolved Pu was captured on the resin during the Cs loading step. Even though Superlig-644 captured the Pu, Pu also readily eluted with the Cs using 0.5 HNO₃. Thus, ~72% of the Pu in supernatant solution from tank AP-101 and 60% of the Pu in AZ-101 supernatant was removed during ion exchange processing with SL-644 (Fiskum et al. (2004b, 2004a); see also Fiskum et al. (2006a, p. 3.15)).

2.2 ARC-359 at the Hanford Site

The Hanford Site used ion exchange processing to recover Cs directly from solution and from solutions derived from tank wastes solids digestion from 1967 until 1979, with continuing purification of the recovered Cs continuing until 1984 (Barton et al. 1986). The operations took place in Hanford’s B Plant following its refurbishment for this task. During the period of operation, two inorganic media (Linde AW-500 and Norton Zeolon-900, both zeolites) and one organic ion-exchange medium (Duolite ARC-359 by Diamond Shamrock) were used. The ARC-359 is a sulfonated phenol-formaldehyde cation exchange resin that, aside from its sulfonate group, shares similarities with the sRF resin in that each attains cation exchange sites in high hydroxide concentration solution via the removal of hydrogen ions from the alcohol (phenol or resorcinol) functional groups.

At Hanford, the ARC-359 resin was loaded in a stainless steel column of 6-foot (1.83 meter) diameter and 2.52–2.88-meter bed height, a volume of ~6.6 to 7.6 m³ (Barton et al. 1986). The column was loaded downflow to Cs breakthrough at ~150 liters/minute, water-washed to remove the interstitial feed solution, scrubbed of sodium ion (Na⁺), which competed with Cs⁺ for loading sites, using 0.15-0.20 M (NH₄)₂CO₃, and eluted downflow with a mixed solution of 2.5-3.0 M (NH₄)₂CO₃ and 1-2 M NH₄OH. The eluate was concentrated in subsequent boil-down and ion exchange processing. The eluted bed was regenerated to the Na⁺ form before loading for the next cycle.

Approximately 30,300 m³ of REDOX waste tank supernatant solution (1.7 M NaOH and ~0.7 Ci ¹³⁷Cs/liter), containing about 20 million Ci of ¹³⁷Cs, were processed over 19 months (Barton et al. 1986). Because typical batch sizes were ~80,000 Ci ¹³⁷Cs, on average, about 25 batches of REDOX supernate were run, each nominally 1200 m³. It is estimated here that at a Pu solution concentration of ~10⁻⁸ M (representative of the solutions tested for RF and sRF; see Table 1), the estimated nominal Pu loading on the column before elution was ~3 grams¹, or a concentration on the ~7-m³ column of 4.1×10⁻⁷ g Pu/mL. At the same time, the nominal Cs loading would have been 0.011 Ci ¹³⁷Cs/mL².

We found no Hanford Site investigations of the fate of dissolved Pu within processing of Hanford Site tank-waste solutions by the ARC-359 in searches of the technical archives, including Hanford's Integrated Document Management System, IDMS, the US Office of Scientific and Technical Information (OSTI), or in Google. However, an analysis of ARC-359 resin thieved from the ion exchange column showed a bulk density of the resin of 0.63 g/mL, 70 μCi ¹³⁷Cs/g (~44 μCi ¹³⁷Cs/mL), and <3.48×10⁻⁷ g ²³⁹Pu/g (<2.2×10⁻⁷ g ²³⁹Pu/mL) (Patterson and Buckingham 1975). Because this "less than" concentration is nearly identical to that postulated by an assumed 100% Pu loading onto ARC-359 resin from REDOX solution of nominal 10⁻⁸ M Pu concentration, no inferences about the affinity of the resin for Pu can be made.

2.3 ARC-359 Studies at the Savannah River Site

Informed by the Hanford Site experience, SRS conducted subsequent studies of ARC-359 resin to remove Cs, strontium, and Pu from alkaline SRS tank wastes in extensive development testing (Wiley (1978); see also Wiley (1976b, 1976a)). In the earlier of these tests, Wiley (1976b) performed batch contact experiments using simulated SRS tank-waste solution. An additional column test used actual tank waste whose composition was adjusted, using reagent chemical addition, to match that of the simulant waste solution. In tests with both simulant and actual waste, ²³⁸Pu spike was added to produce 10⁻⁶ M ²³⁸Pu and the spiked solution allowed two weeks to attain equilibrium. Because no description of solution filtration was provided in the report, it is not known whether solution clarification was performed. However, the 0.3 M carbonate also present in the solution would have been sufficient to dissolve the Pu.

Table 4 shows the test solution compositions and the decontamination factors (DFs) from Pu. The initial batch test (with simulant waste) and the column test (with actual waste amended to attain the same bulk waste composition) demonstrated relatively high Pu removal rates. In the initial batch test with simulant waste, the distribution coefficient, K_d,—the amount of Pu per gram of resin after contact of the (1 g of) resin with (the 10 mL of) solution divided by the amount of Pu per milliliter remaining in solution after contact—was 180 mL/g. The Pu DF achieved in this batch contact thus was 19; i.e., Pu concentration in solution decreased by a factor of 19 after contact with the resin. SRS researchers then studied the effects of NaOH and NaNO₃ concentration in the simulant on Pu uptake by the ARC-359 resin. They found that as the NaOH concentration in the simulant increased from 0.75 M to 3.75 M (all other bulk chemical concentrations remaining roughly equivalent), the Pu distribution to the resin decreased, with K_ds diminishing from 240 to 65. They noted a similar decrease in Pu uptake (K_d decrease from 240 to 46) when the NaNO₃ concentration increased from 2.2 to 5.2 M.

¹ 1.2×10⁶ liters × 10⁻⁸ moles Pu/liter × 239 g Pu/mole Pu

² 80,000 Ci/7×10⁶ mL

Twenty column volumes (CV) of solution were passed through a CV of ARC-359 resin in the single column test, run with ^{238}Pu -spiked and chemically amended actual waste. The Pu concentration of the solution that passed through the column was 500 times lower than that of the feed solution—i.e., the DF was 500. Assuming a resin bulk density of 0.5 g/mL, the K_d in the column test was $\sim 20,000$ mL/g. The much higher K_d compared with the batch tests reflects the successive incrementally stepwise equilibria of Pu uptake onto the ARC-359 resin as the solution passed through the column. Under the column loading conditions, diminishing Pu concentrations would be experienced by the resin particles deeper in the bed, thus compounding the K_d . Elution of the Pu from the column was facile and complete using a mixture of 2.0 M $(\text{NH}_4)_2\text{CO}_3$ with 2 M NH_4OH , similar to the Cs eluent used at Hanford.

Wiley (1976a, 1978) soon followed up with nine additional column tests with two different actual SRS tank-waste solutions. Supernatant solution from Tank 15H was used in the first three tests, and Tank 34F supernate in the remaining tests. The bulk chemical composition used in all nine tests was practically identical to the compositions used in the earlier (Wiley 1976b) tests, made that way by addition of reagent salts to attain the target composition. In seven of the tests, the actual waste solution also was contacted with actual waste sludges taken from various tanks to simulate the waste retrieval process. It seems (based on Table II of Wiley 1978 Wiley (1978)) that the sludges used were not the same from one test to the next. The solution to be used in the column testing then was clarified by centrifugation and filtration through two sand/anthracite beds. In the ion-exchange testing, the actual waste solution was passed, in series, through two 2.5-liter volume ARC-359 resin columns and, for some tests, a third column of Chelex 100 resin to capture dissolved strontium. From 20 to 60 CVs were run in these tests at rates varying from 1 to 3 CV/hour (higher rates, in general, for the higher throughputs). As in the prior SRS testing, (Wiley 1976b) eluted both Cs and Pu using 2.0 M $(\text{NH}_4)_2\text{CO}_3$ with 2 M NH_4OH (Wiley 1976a, 1978).

Pu present in the waste solutions themselves was used to elucidate Pu behavior for eight of the nine tests (Wiley 1976a, 1978). Unfortunately, Pu concentration measurements for two of these column tests (the fifth and sixth using waste from Tank 34F) were unreliable, including the 60 CV test run at 3 CV/hour, and are not considered in the present analysis. Because the researchers suspected that background Pu contamination from the hot cell in which the experiments were performed contributed to unreliably low measured DFs in the initial eight tests, the ninth test was performed by spiking the actual waste to 1.5×10^7 DPM (disintegrations per minute)/mL in ^{238}Pu . The column feed and effluent Pu concentrations were reported in DPM per milliliter of solution, but Pu isotopic compositions were not reported.

For the purposes of the present report, the Pu concentrations in the SRS tests were estimated as if the SRS tank waste Pu had approximately the same weapons-grade isotopic composition as that of the Hanford Site tank waste (as shown in footnote a in Table 1) and thus had a specific alpha activity of 0.0752 Ci $^{238,239,240}\text{Pu}$ /g Pu. Based on this specific activity, calculation shows $\sim 5 \times 10^{-7}$ M Pu present in the first eight tests and $\sim 2 \times 10^{-6}$ M Pu in the ninth test. However, higher specific Pu isotopic activity could very plausibly be true if the waste solutions contained residues from the ^{238}Pu production that occurred in the SRS H Canyon or residues from other activities with high-specific-activity Pu isotopes. If the ^{238}Pu fraction in the SRS tank-waste feed solutions were greater than the ~ 0.02 wt% present in average Hanford waste, the specific activity would be higher and the Pu molar concentrations lower than projected.

The DFs in the six considered non-spiked tests ranged from 5 to 60, but the variability is uncorrelated with the waste solution throughput quantities, throughput rates, or waste solution origin. The ^{238}Pu -spiked

test showed a Pu DF of 300, in better agreement with the prior lab-scale column testing where the DF from Pu was 500 (Wiley 1976b).

Table 4 summarizes the results of the initial (Wiley 1976b) and the subsequent (Wiley 1976a, 1978) SRS tests of ARC-359 resin. These studies—particularly the latter column tests in which the feed solution is known to have been filtered—demonstrate that Pu is quantitatively removed from alkaline nitrate-bearing waste solution of composition similar to that found in the Hanford radioactive waste tanks.

Table 4. Results of Pu Ion-Exchange Tests onto ARC-359 Performed at SRS

Expt. Parameters	Savannah River Laboratory Test Conditions										
	Simulant	Actual	Simulant	Simulant	Actual						
	Batch	Column	Batch	Batch	Column						
NaOH, M	0.75	0.75	0.75/1.75/ 2.75/3.75	0.75	0.75 – 1.0						
NaNO ₃ , M	2.2	2.2	2.2	2.2/3.2/ 4.3/5.2	2.2						
NaNO ₂ , M	1.1	1.1	1.1	1.1	1.1						
NaAlO ₂ , M	0.50	0.50	0.50	0.50	0.5						
Na ₂ SO ₄ , M	0.3	0.3	0.3	0.3	0.3						
Na ₂ CO ₃ , M	0.3	0.3	0.3	0.3	0.3						
Total Pu, M	10 ⁻⁶	Est. 10 ⁻⁶	10 ⁻⁶	10 ⁻⁶	Estimated ~5×10 ⁻⁷						~2×10 ⁻⁶
Condition	10 mL/g	20 CV	Unstated; assume 10 mL/g		20	20	30	40	40	40	20
					CV						
Pu K _d , mL/g	180	20,000	240/136/ 76/65	240/242/ 49/46	236 0	280	160	148 0	116 0	164 0	11,960
DF	19	500	25/14.6/ 8.6/7.5	25/25.2/ 5.9/5.6	60	8	5	38	30	42	300
Reference	(Wiley 1976b) ^a		(Wiley 1976b) ^b	(Wiley 1976b) ^c	(Wiley 1976a, 1978) ^d						

Pu K_d batch contact values calculated from DF column test values and DFs calculated from K_ds are indicated in shaded cells
a – Tests in both cases included 10⁻⁶ M Pu added as ²³⁸Pu. The Pu concentration in the actual waste is not known. The composition of the actual waste was adjusted with non-radioactive chemicals to match that of the simulant.
b – Solid NaOH added to achieve 1.75, 2.75, and 3.75 M NaOH in the three more concentrated simulants. Small dilutions of other component concentrations occurred but were not accounted. 10⁻⁶ M Pu added as ²³⁸Pu.
c – Solid NaNO₃ added to achieve 3.2, 4.2, and 5.2 M NaNO₃ in the three more concentrated simulants. Small dilutions of other component concentrations occurred but were not accounted. 10⁻⁶ M Pu added as ²³⁸Pu.
d – Input Pu concentrations for these six tests were averaged (~21,000 DPM total ^{238,239,240}Pu α/mL) and the isotopic composition assumed to be the same as that for Hanford Site wastes (see Table 1, footnote a). Two other column tests were reported but are not provided here because of Pu feed concentration anomalies. To overcome postulated hot cell contamination problems, ²³⁸Pu spike was added to the final input test solution to saturation, giving 1.5×10⁷ DPM ²³⁸Pu/mL (~1.7×10⁻⁶ M) + 5×10⁻⁷ M existing Pu concentration in waste for an estimated total 2×10⁻⁶ M Pu

2.4 Los Alamos National Laboratory Survey Studies

In 1991-1995, Marsh, Svitra, and colleagues at the Los Alamos National Laboratory (LANL) conducted an extensive set of batch contact experiments to determine radionuclide uptake from simulated alkaline, diluted, and acidified Hanford Site tank-waste solutions onto commercial and developmental ion-exchange and solid-phase sorption media. The results of these studies were presented in a series of topical reports (LA-12528, -12654 Rev, -12862, -12863, -12889, -12943, and -13000). Among the radioelements investigated was Pu but only the last of these many reports from this team (Marsh et al. 1995) detailed studies for Pu uptake from alkaline solution.

The 33 solid phase media investigated in this last set of testing included both inorganic and organic substrates. Among the organic media tested were Superlig-644 and the RF resin BSC-210 from Boulder Scientific Company. While Marsh and colleagues (1995) undertook no studies using the ARC-359 that had been custom-made for Hanford application and had been investigated for SRS use, they did study Duolite CS-100. The CS-100 is a granular weak-acid phenol-formaldehyde cation exchange resin and thus related to the Duolite ARC-359 used in Hanford operations.

Marsh et al. (1995) prepared a water-diluted “complexed concentrate” simulant waste solution for testing. This waste contained six organic complexing agents – EDTA, HEDTA, NTA, citrate, gluconate, and iminodiacetate.¹ Separate portions of the simulant waste solution then underwent radiolysis (to 34 megarad, Mrad, or 3.4×10^5 Gray, total absorbed gamma dose from cobalt-60), hydrothermal treatment at 450°C under 15,000 psi (~1000 bar) pressure for 25 seconds, and both 34 Mrad irradiation and 450°C hydrothermal treatment. Each of the four simulants were filtered and then spiked with various trace radioactive species, including ^{238}Pu at a level of 10 mg/liter, equivalent to 4.2×10^{-5} M. After at least one week to allow for spike dissolution to occur, the simulant waste solution again was filtered (0.45 μm pore-size filters in both cases). The concentration of ^{238}Pu remaining dissolved was not reported. The analyzed compositions of the four test solutions, copied from Table 1 of the original report (Marsh et al. 1995), show that the pH was relatively low, equivalent to ~0.16 M NaOH without hydrothermal treatment and ~0.01 M NaOH after hydrothermal treatment.

¹ EDTA is ethylenediaminetetraacetate – $(\text{O}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2^-)_2$;
HEDTA is N-2-hydroxyethyl ethylenediaminetriacetate – $(\text{O}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2^-)(\text{CH}_2\text{CH}_2\text{OH})$;
NTA is nitrilotriacetate – $\text{N}(\text{CH}_2\text{CO}_2^-)_3$; citrate is $\text{O}_2\text{CCH}_2\text{C}(\text{OH})(\text{CO}_2^-)\text{CH}_2\text{CO}_2^-$; gluconate is $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2^-$; and iminodiacetate is $(\text{O}_2\text{CCH}_2)_2\text{NH}$.

Table 1. Compositions of the Four Variations of Diluted^a Generic Hanford CC Simulant Solutions

Constituent	Concentration (M)			
	Unirradiated/ untreated	Irradiated/ untreated	Unirradiated/ hydrothermal-treated	Irradiated/ hydrothermal-treated
Cations^b				
Na	2.2	2.1	1.9	1.6
K	0.009	0.009	0.013	0.014
Rb	1.3×10^{-5}	1.2×10^{-5}	9×10^{-6}	1.0×10^{-5}
Cs	1.4×10^{-4}	1.3×10^{-4}	1.0×10^{-4}	1.3×10^{-4}
Al	0.16	0.16	0.024	0.012
Ca	0.002	0.002	0.0001	0.0001
Fe	0.003	0.005	6×10^{-5}	7×10^{-5}
Sr	1.3×10^{-4}	1.3×10^{-4}	3×10^{-5}	3×10^{-5}
Anions^c				
Cl	0.04	0.012	0.012	0.013
NO ₃	0.9	0.9	0.5	0.7
NO ₂	0.3	0.3	0.1	0.1
PO ₄	0.009	0.009	BDL ^d	BDL
SO ₄	0.006	0.007	0.003	0.003
CO ₃	0.19	0.23	0.49	0.62
TOC ^e	1.0	0.9	0.13	0.14
pH	13.2	13.2	11.9	12.1

^aDilutions consisted of three volumes of water to one volume of undiluted simulant.
^bCations, except Na and K, were measured by inductively coupled plasma/mass spectrometry (ICP/MS).
^cAnions, as well as Na and K cations, were measured by ion chromatography (IC).
^dBelow detection limit.
^eTotal organic carbon.

Figure 2. Compositions of Simulated Complexed Concentrate Waste Solutions Used in LANL Tests (Table 1 of Marsh et al. (1995))

Figure 3 (from Table 8 of Marsh and colleagues (1995)) shows the best performing Pu absorbers for the four test solutions. Neither the Superlig-644 nor the RF resin BSC-210 merited mention in this summary table, while the phenol-formaldehyde resin CS-100 provided K_{ds} ranging from about 5 to 16 mL/g after 6 hours of contact, depending on solution. The K_{ds} increased with hydrothermal treatment, but not with irradiation. Table 24 of Marsh and colleagues (1995) provides further detail for BSC-210, showing Pu K_{ds} of 0.4 mL/g and lower; Superlig-644 had Pu K_{ds} of 0.2 mL/g and lower (Table 35 of Marsh et al. (1995)).

However, the 6-hour K_d values of 5.3 and 5.2 mL/g for CS-100 presented in Figure 3 (Table 8 from Marsh et al. (1995)) for the tests of solution that did not undergo hydrothermal treatment are higher than those (K_d of 0.1 mL/g and below at 6 hours of contact) provided in Figure 4 (from Table 15 of Marsh et al. (1995)) for the same tests. It is not evident which set of values is correct.

Table 8. Plutonium Distribution Data—Kd Values for Sorption of Plutonium from Four Variations of 3:1 Diluted Generic Hanford CC Simulant Solution

Absorber	Unirradiated/ untreated			Irradiated/ untreated			Unirradiated/ hydrothermal-treated			Irradiated/ hydrothermal-treated		
	30 min	2 h	6 h	30 min	2 h	6 h	30 min	2 h	6 h	30 min	2 h	6 h
Duolite™ CS-100	2.2	3.7	5.3	2.0	3.7	5.2	9.2	13	16	4.9	6.6	8.8
Ionsiv™ IE-910 (CST)	1.0	2.1	3.7	0.8	1.7	3.0	0.3	0.2	0.3	0.2	0.3	0.4
SNL/HTO	0.7	1.2	2.4	0.1	0.1	0.8	564	753	1036	271	349	430
Bone char	0.5	0.4	0.4	<0.1	0.3	0.1	138	357	519	81	169	265
KCoFC crystals	0.5	0.4	0.5	<0.1	0.1	0.2	6.9	7.4	8.0	2.9	3.0	3.6
KCoFC-PAN	0.5	0.5	0.6	<0.1	<0.1	<0.1	2.8	4.4	6.3	0.4	1.3	1.7
Aliquat™ 336	0.4	0.3	0.3	<0.1	<0.1	<0.1	0.5	0.3	0.2	<0.1	<0.1	<0.1
NiFC-PAN	0.4	0.3	0.4	<0.1	<0.1	<0.1	1.2	2.0	3.6	<0.1	0.3	0.9
Cyanex™ 923	0.4	0.3	0.3	<0.1	<0.1	<0.1	0.3	0.4	0.3	0.3	0.3	0.2
Clinoptilolite	0.3	0.4	0.3	<0.1	0.2	0.2	2.3	2.2	2.2	0.9	0.7	0.7
Na nanotitanate (8104-170)	0.3	0.4	0.5	0.2	<0.1	<0.1	269	439	656	98	168	244
Tannin	0.2	<0.1	0.2	0.5	0.2	0.4	43	378	1714	22	170	552
Na nanotitanate (8225-127)	<0.1	0.3	0.3	<0.1	<0.1	0.1	201	350	477	97	160	201
UTEVA-Spec™	<0.1	<0.1	<0.1	0.5	0.6	0.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TRU-Spec™	<0.1	<0.1	<0.1	0.1	0.4	0.3	<0.1	<0.1	<0.1	0.2	0.1	0.1

Figure 3. Pu Distribution Data for Better-Performing Sorbents in LANL Testing (Table 8 of Marsh et al. (1995))

Table 15. Distribution of Five Elements onto Duolite™ CS-100 Cation Exchange Resin from a 3:1 Dilution of Four Variations of Generic Hanford CC Simulant Solution

Element	Kd Value for Specified Time					
	Unirradiated/ untreated			Irradiated/ untreated		
	30 min	2 h	6 h	30 min	2 h	6 h
Am	<0.1 ± 0.0	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.3 ± 0.3	0.2 ± 0.2
Cs	116 ± 1.9	131 ± 1.2	126 ± 0.2	93 ± 0.0	111 ± 0.5	104 ± 2.6
Pu	0.3 ± 0.1	<0.1 ± 0.0	0.1 ± 0.1	<0.1 ± 0.0	<0.1 ± 0.0	<0.1 ± 0.0
Sr	0.7 ± 0.1	0.9 ± 0.0	1.0 ± 0.0	0.4 ± 0.2	1.1 ± 0.2	1.1 ± 0.1
Tc	0.5 ± 0.1	0.6 ± 0.0	0.6 ± 0.0	0.5 ± 0.2	1.0 ± 0.3	0.8 ± 0.0

Element	Unirradiated/ hydrothermal-treated			Irradiated/ hydrothermal-treated		
	30 min	2 h	6 h	30 min	2 h	6 h
	Am	12 ± 0.4	84 ± 19	571 ± 55	5.9 ± 0.0	41 ± 5.6
Cs	45 ± 0.5	50 ± 0.8	50 ± 0.3	41 ± 0.1	46 ± 0.2	47 ± 0.5
Pu	9.2 ± 0.5	13 ± 0.8	16 ± 1.0	4.9 ± 0.2	6.6 ± 0.1	8.8 ± 0.0
Sr	21 ± 0.3	44 ± 5.0	77 ± 6.5	14 ± 0.3	34 ± 1.6	63 ± 2.1
Tc	0.3 ± 0.3	0.2 ± 0.0	0.2 ± 0.0	0.3 ± 0.1	0.6 ± 0.1	0.7 ± 0.0

Figure 4. Pu Distribution onto CS-100 from Diluted Complexant Concentrate Simulant Waste Solution (Table 15 of Marsh et al. (1995))

Marsh and colleagues (1995) conducted further testing of several of the more promising ion exchangers and sorbents (including CS-100) using “complexed concentrate” simulant waste solution diluted at a 1:1 ratio using 1 M NaOH rather than water. The diluted solutions contained ~0.6 M NaOH (derived from Table 55 of Marsh et al. (1995)). Two solution types, non-irradiated and irradiated, were prepared. But the results for CS-100 using the solutions containing ~1 M NaOH (reported in Table 46 of Marsh et al. (1995)) were very similar to those found in the water-diluted tests having ~0.16 M NaOH, showing K_{ds} of 0.1 mL/g and lower. The RF resin BSC-210 had Pu K_{ds} of 0.4 and lower, as did Superlig-644 (Tables 51

and 54, respectively, of Marsh et al. (1995)), virtually indistinguishable from the findings of the water-diluted simulant (Tables 24 and 35, respectively, of Marsh et al. (1995)).

Overall, Marsh and colleagues (1995) found negligible Pu uptake from simulated dilute complexed concentrate waste onto phenol-formaldehyde resin (CS-100), RF resin (BSC-210), or crown ether-type resin (Superlig-644) of concern in the present investigation of the behavior of the sRF resin. Incidentally, of the sorbents tested, the greatest Pu uptake was shown by various titanates and by bone char (Figure 3, taken from Table 8 of Marsh et al. (1995)).

3.0 Bases for Criticality Concerns by Pu Uptake onto sRF

Concern about the disposition of Pu in ion exchange (IX) processing to remove Cs from alkaline radioactive waste solution was expressed in the Preliminary Criticality Safety Evaluation Report for the WTP as shown below, page A-2 of (Miles 2009):

A.1.4 Verify that Pu and Metals Accumulate Together on the IX Resin

The criticality safety of IX processing is established by demonstrating that sufficient metals are held up with the Pu on the resin to ensure CSL 8.4 compliance. More data, probably from experiments, are needed for demonstrating IX resin holdup of Pu and absorbers. Similar data on IX resin holdup are presented in Table 4-2, but data that are more detailed are needed. The new data should provide understanding of how oxidative leach and consequent changes in Pu oxidation state may affect Pu holdup. Study also needs to verify that the Pu and absorber metals accumulate in the same regions of the resin.

Created 11/2006 and subsequently modified.

In fact, concerns regarding the criticality safety in the IX column were expressed as early as 2006, before the experimental results of Fiskum and colleagues (2009) and Nash and Duignan (2010) further elevated the issue.

Criticality concerns arising from the observed Pu uptake onto sRF resin from actual alkaline radioactive waste solution by PNNL (Fiskum et al. 2009) and especially SRNL (Nash and Duignan 2010) were summarized by Losey (2016a), the WRPS Criticality Safety Engineer (see Appendix A). As Section 1.2.2 of the present report shows regarding testing of dissolved SRS saltcake waste by Nash and Duignan (2010), 38% of the feed Pu was retained by the sRF resin during Cs loading with 10% of the input Pu still remaining on the resin after elution using 0.5 M HNO₃.

In these considerations for a preliminary criticality safety evaluation report (CSER) for the low-activity waste pretreatment system (LAWPS), Losey (2016a) assumed a worst-case (i.e., highest) ²³⁹Pu concentration in the feed solution to the WTP of 3×10⁻⁵ Ci ²³⁹Pu/L (or 2.15×10⁻⁶ M total Pu).¹ This upper limit is specified by the Interface Control Document (ICD) for direct low-activity waste feed to the WTP (Schappell 2015).

Losey (2016a) also adopted the 360-g WTP criticality safe mass limit for ²³⁹Pu. This conservative Pu mass limit assumes optimal geometry and neutron moderation (Miles 2008). While the 360-g limit is a preliminary value and might be increased a factor of 3 to 4 with calculation refinement, it nevertheless represents a conservative starting point for criticality considerations.

Losey (2016a) then assumed hypothetical but plausible Cs IX process feed rate of ~64 liters/minute (17 gallons per minute) at the ICD maximum 0.5 mg Pu/L concentration. Under these conditions, 38% Pu

¹ $\frac{3 \times 10^{-5} \text{ Ci } ^{239}\text{Pu}}{\text{liter}} \times \frac{\text{g } ^{239}\text{Pu}}{0.06203 \text{ Ci } ^{239}\text{Pu}} \times \frac{\text{g Pu total}}{0.93915 \text{ g } ^{239}\text{Pu}} \times \frac{\text{mole Pu}}{239.11 \text{ g Pu}} = 2.15 \times 10^{-6} \text{ M}$, based on the Pu composition given in footnote a of Table 1

loading would capture 352 g of Pu after 20 days of continuous IX loading operation and thus closely approach the 360-g safe limit. It is noted, however, that routine operations necessitated by Cs breakthrough characteristics would cause much more frequent elution. The typical envisioned elution frequency is after 3-4 days of operation. If the loaded column then were eluted and the Pu retained on the column after elution were the same 10% of input as observed by Nash and Duignan (2010), about 92 g of Pu would be carried over for the next loading cycle. Even neglecting the Pu retained during the second resin loading step and the resulting collection of (92 + 352 =) 444 g of Pu at the completion of the second loading assuming the same process parameters as the first loading, only four cycles of 92-g retentions (i.e., 368 g Pu total) would be required to exceed the 360-gram criticality safe mass limit.

As noted by Losey (2016a), consideration had previously been given to the WTP criticality concern arising from the observed Pu uptake onto the Cs ion-exchange columns (Delegard et al. 2015). In this study, the authors remarked on page 2.8 that “dissolved plutonium species in alkaline waste are anionic (negatively charged) and highly unlikely to be attracted to the IX media, which are designed to attract the positively charged Cs ion, Cs⁺”.

Therefore, Losey (2016a) suggested that something besides ion-exchange charge attraction could be responsible for the Pu uptake on the sRF resin. For example, if the Pu were present in particulate form, uptake onto the sRF resin might include filtration, electrostatic particle-particle attraction, or surface adsorption of the Pu-bearing particles onto the resin. He noted that while the SRS test feed was filtered to 0.2 μm (Nash and Duignan 2010) and the LAWPS feed would be filtered to 0.1 μm in the crossflow ultrafilters, the size of “Pu(OH)₄” coprecipitated onto iron (Fe) phase particles is 0.02 μm (stated as 0.015 μm in Table 4-1 of Tardiff (2016) as taken from Table 3.14 of Wells et al. (2011)). It should be pointed out that, for the most part, bed filtration (i.e., capture of particles not by the filter medium itself, but by the bed of particles collected above the filter medium) occurs. However, it is possible that in the absence of bed filtration, Pu in the “clarified” feed in the SRS testing as well as in the PNNL testing (Fiskum et al. 2009) might have been present not as dissolved species but rather as small particles.

Losey (2016a) predicted passage of particles, as functions of their size, through a bed of the monodisperse sRF (shown in Figure 5). As Figure 5 shows, the optimum particle size to pass through the resin column lies at ~1 μm. Nash and Duignan (2010) used a ~6.5-cm sRF bed depth. According to the plots in Figure 5, perhaps 6% of the nominal 0.02 μm Pu-bearing iron oxide/hydroxide particles would have been retained in a 6.5-cm bed depth. This result is of the same order of magnitude as the Pu capture fraction observed by Fiskum and colleagues (2009) and Nash and Duignan (2010).

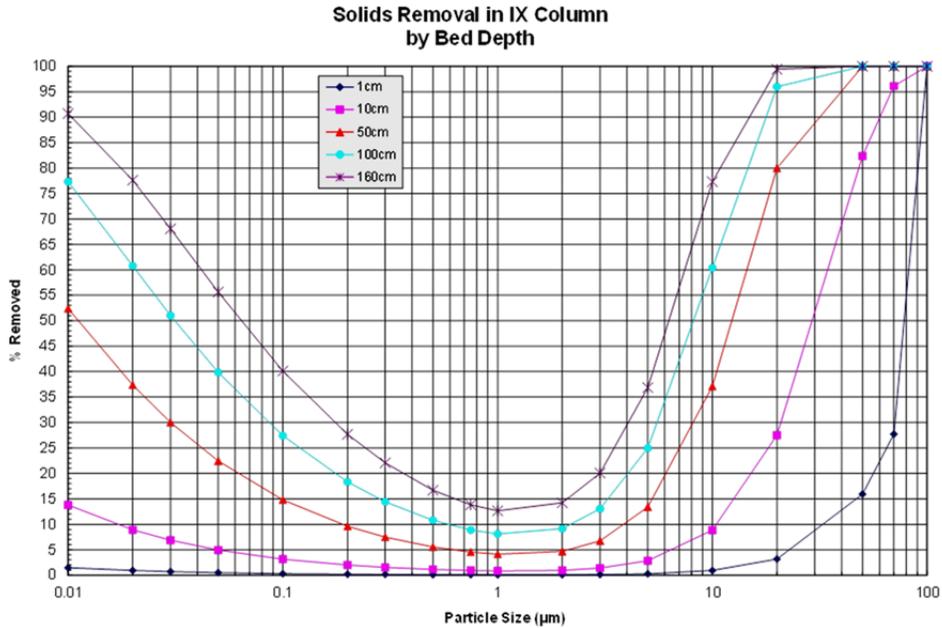


Figure 5. Solid Particle Retention by sRF Resin Column as Functions of Bed Depth and Particle Size (Losey 2016a)

A subsequent Preliminary Criticality Safety Evaluation Report for the LAWPS was released in June 2016 (Losey 2016b). This assessment further defines the issues arising from the sRF testing and on page 28 states:

Assumption 6.2.4 Resin Pu Retention Mechanism – As discussed with Upset 5.3.4, the mechanisms by which Pu is retained on the IX resin is not well understood. The Pu dissolved in caustic waste is anionic, while sRF resin is a cation-sorbing resin used for ¹³⁷Cs removal. Thus, ion exchange sorption of Pu by the resin is expected to be negligible. Because some testing has shown unexpected Pu retention, further understanding of the mechanisms is needed. An assumption is that further investigation into the Pu retention will be done in support of finalizing a LAWPS CSER.

4.0 Overview of Pu Chemistry in Hanford Tank Wastes

The chemical behavior and properties of Pu in the alkaline Hanford tank-waste media was the subject of a recent review prepared for the WTP (Delegard and Jones 2015). The review examined and summarized the findings from numerous studies at the Hanford and Savannah River Sites, in the Soviet Union and Russia, in France, and elsewhere on the observed and postulated chemical disposition of Pu in Hanford and Savannah River Site tank wastes and in alkaline systems similar to Hanford tank wastes, by itself and in its interactions with the selected neutron absorber elements aluminum (Al), bismuth (Bi), cadmium (Cd), chromium (Cr), iron (Fe), manganese (Mn), nickel (Ni), sodium (Na), and uranium (U). The review investigated Hanford Site Pu processes to provide an overview of Hanford tank defined-waste-type compositions and calculate the ratios of Pu to absorber elements in these waste types and in individual waste analyses. Most importantly for the present issues of Pu uptake onto sRF resin, this work described the distribution and expected speciation of Pu in tank-waste solution and solid phases. The following discussion, unless otherwise noted, arises from information presented in that review and in the many references cited therein.

4.1 Pu Oxidation States and Oxidation/Reduction Reactions in Solution

Pu is a multi-valent element with five oxidation states accessible in aqueous solution—III, IV, V, VI, and VII. The existence of a VIII oxidation state is subject to debate and will not be considered in the present discussion. If it does exist, it requires extravagantly oxidizing conditions well beyond those available in waste storage or processing. Of the five available oxidation states, both III and VII are practically inaccessible in stored Hanford tank-waste solution, as they are unstable to reductive and oxidative decomposition of water to hydrogen gas (H_2) and oxygen gas (O_2), respectively. Progression from the IV to the V and then VI states requires increasingly oxidizing conditions. In NaOH solution below about 6 M, the V oxidation state is unstable to disproportionation to form Pu(IV) and Pu(VI). The low solubility of Pu(IV) in NaOH solution means that disproportionation usually is accompanied by formation of the low-solubility hydrated Pu(IV) oxide solid phase, $PuO_2 \cdot xH_2O$, rather than dissolved Pu(IV).

Figure 6 presents an informative way to visualize the accessibility of the various Pu oxidation states in alkaline solution. For example, note that the electrode potential necessary to oxidize Pu(VI) to Pu(VII) in 1 M NaOH is about 0.85 V, whereas the potential needed to oxidize water to oxygen is 0.401 V (Bratsch 1989). Therefore, Pu(VII) is highly unstable in 1 M NaOH, evidenced by the fact that it can react with water to form O_2 . Also shown in Figure 6 are oxidation/reduction (redox) electrochemical couples for several pairs of major tank-waste species, such as the ubiquitous nitrate/nitrite (NO_3^-/NO_2^-) or the less common chromate/chromium hydroxide ($CrO_4^{2-}/Cr(OH)_3$ ppt). These redox couples may control the electrochemical state of the Hanford tank-waste solutions. Based on the position of the NO_3^-/NO_2^- couple at 0.017 V, being well in the field of Pu(IV) stability, Pu(IV) is highly favored in stored Hanford tank waste. However, under oxidative leaching conditions using permanganate, MnO_4^- (0.56 V in equilibrium with MnO_4^{2-}), Pu(IV) can readily be oxidized to Pu(VI).

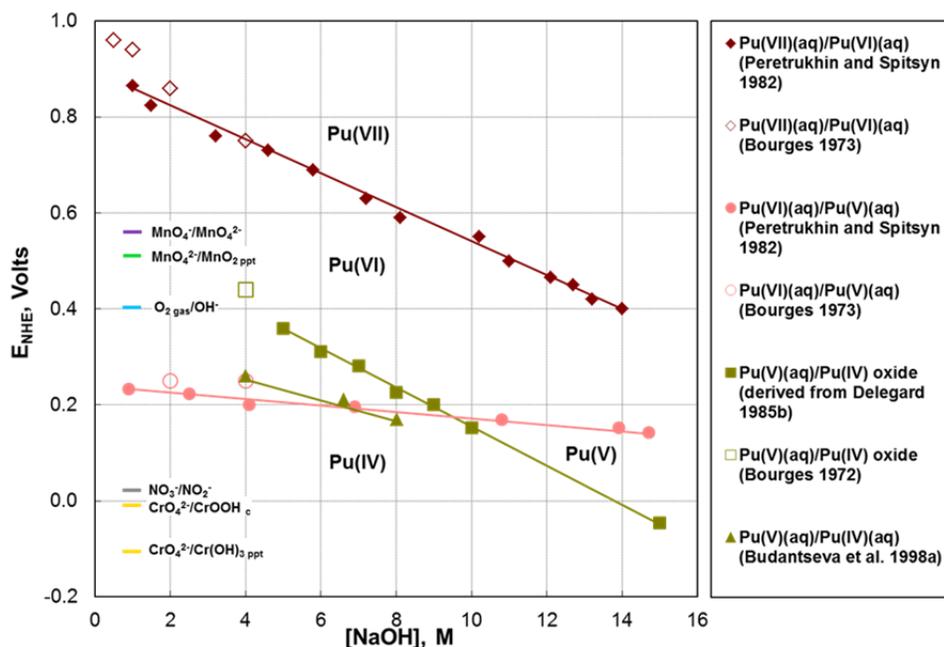


Figure 6. Pu Reduction/Oxidation Potentials in NaOH Solution (right panel: bibliographic information is found in Delegard and Jones (2015))

Figure 6 also shows that the $\text{Pu(V)}_{(\text{aq})}/\text{PuO}_2 \cdot x\text{H}_2\text{O}$ and $\text{Pu(V)}_{(\text{aq})}/\text{Pu(IV)}_{(\text{aq})}$ potentials cross the plot of the $\text{Pu(VI)}_{(\text{aq})}/\text{Pu(V)}_{(\text{aq})}$ potentials at ~ 9.5 M NaOH and ~ 6.5 M NaOH, respectively. These crossings indicate that Pu(V) is unstable to disproportionation to form $\text{Pu(IV)}_{(\text{aq})}$ or $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ and $\text{Pu(VI)}_{(\text{aq})}$ at NaOH concentrations lower than the respective crossing points. Further, Pu(VI) is not stable indefinitely in NaOH solution. With time, perhaps due to alpha (α) radiolytic reactions to form chemical reducing agents, the Pu(VI) will be reduced to Pu(V), and disproportionate to Pu(VI) and Pu(IV), or reduce further to Pu(IV) and precipitate to form $\text{PuO}_2 \cdot x\text{H}_2\text{O}$.

4.2 Solubility of Pu Solid Phases in Alkaline Media and as a Function of pH

The solubilities of Pu hydrated oxide solids and its sodium salts in NaOH solution are dramatically influenced by the oxidation state of the solid. As shown in Figure 7, the solubility increases greatly with increase in oxidation state. For example, at 5 M NaOH, the solubility of the Pu(IV) solid phase, which is $\text{PuO}_2 \cdot x\text{H}_2\text{O}$, is about 10^{-6} M, the solubility of the Pu(V) solid phase, perhaps $\text{Na}_3\text{PuO}_2(\text{OH})_4$, is about 100 times greater at 10^{-4} M, and the Pu(VI) solid phase, perhaps $\text{Na}_2\text{PuO}_2(\text{OH})_4$, has solubility another 100 times greater, or about 10^{-2} M.

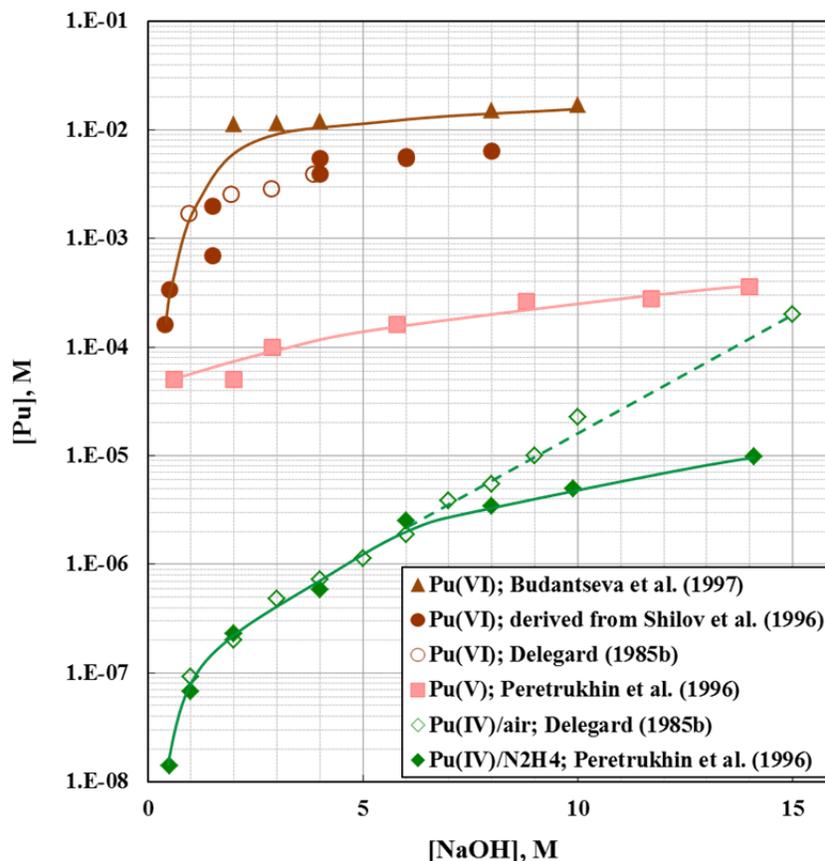


Figure 7. Pu Compound Solubilities as Functions of Oxidation State and NaOH Concentration (bibliographic information is found in Delegard and Jones (2015))

The solubilities of the various Pu solid phases also increase with an increase in NaOH concentration. For example, the solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ increases from about 10^{-8} M in 0.5 M NaOH to about 2×10^{-4} M in aerated 15 M NaOH (Figure 7). The solubility of the Pu(VI) phase(s) rises steeply from 0.3 to 3 M NaOH, but then levels off at higher NaOH concentrations. The solubility of the Pu(V) phases in NaOH solution increases nearly an order of magnitude as NaOH concentration increases from 0.5 to 14 M. As Figure 7 shows, the solubility line for $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ splits at about 6 M NaOH, depending on whether the solution is in the presence of only air or air with hydrazine (N_2H_4) added as a chemical reductant.¹ At and below 6 M NaOH, the presence of hydrazine has no influence on the observed solubility. Above 6 M NaOH, the $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ solubility is lower with hydrazine than without it. The dissolved Pu is in the (V) oxidation state in the aerated solutions at 10 M and 15 M NaOH as determined by spectrophotometry, and is in an oxidized state ((V) or (VI) rather than (IV)) at 5 M NaOH. Thus, hydrazine seemingly prevents the $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ from oxidatively dissolving as a Pu(V) species. This behavior is consonant with the observed redox stability of Pu(V) in solution above 6 M NaOH.

The increasing solubilities of Pu(IV), Pu(V), and Pu(VI) with increasing NaOH concentration indicate that the dissolved Pu species are anionic hydroxide complexes such as $\text{Pu}(\text{OH})_5^-$ for Pu(IV), $\text{PuO}_2(\text{OH})_4^{3-}$

¹ Hydrazine is a very strong reductant. The potential of the $\text{N}_2/\text{N}_2\text{H}_4$ couple at pH 14 is -1.160 V, whereas the potential of the water reduction couple, $\text{H}_2\text{O}/\text{H}_2$, is -0.828 V—S. G. Bratsch, *Standard Electrode Potentials and Temperature Coefficients in Water at 298.15 K*, *Journal of Physical and Chemical Reference Data* 18.1 (1989).

for Pu(V), and $\text{PuO}_2(\text{OH})_4^{2-}$ for Pu(VI). However, that strong arguments against the existence of $\text{Pu}(\text{OH})_5^-$ have been made based on the lack of observation of analogous anionic Th(IV) hydroxide complexes that would be manifested by increasing solubility in NaOH solution as well as lack of evidence for analogous anionic U(IV) and Np(IV) hydroxide complexes (Ryan and Rai 1987).

As summarized by Delegard and Jones (2015), various tests of the effects of other dissolved Hanford Site tank-waste components (sodium salts of hydroxide, nitrate, nitrite, aluminate, carbonate, phosphate, sulfate, fluoride, chromate, ferrocyanide, silicate, EDTA, HEDTA, citrate, and glycolate) at nominal waste concentrations on the solubility of Pu solid phases in alkaline solution have been done. Nitrate and nitrite, because of their relatively high concentrations in Hanford waste, appear to increase solubility slightly by ionic strength effects on the hydroxide chemical activity, whereas nitrite, without nitrate, was found to decrease Pu concentrations slightly, perhaps by inhibiting oxidation of Pu to more soluble higher oxidation states. Aluminate may, and carbonate certainly does, increase solubility by complexation. Statistically-designed parametric testing performed at SRNL (Rudisill et al. 2009) produced a modeling equation that predicts with some accuracy the solubility of Pu solids in simulated alkaline tank-waste solutions. Factors in the equation include concentrations of hydroxide, carbonate, aluminate, and nitrite. Silicate increases Pu solid-phase solubility at low (sub-molar) NaOH concentrations (Shilov and Fedoseev 2003). None of the organic waste constituents, even EDTA, appears to influence Pu solid-phase solubility in molar hydroxide solution. In the presence of nearly all of the anions listed at the beginning of this paragraph, the solid phase that forms is $\text{PuO}_2 \cdot x\text{H}_2\text{O}$. However, at higher NaOH concentrations and in the presence of silicate or phosphate, evidence exists for formation of silicate- and phosphate-bearing Pu solid phases (Yusov et al. 2000), whose solubility should be lower than that of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$.

Figure 8 shows the effects of pH, from highly acid to highly alkaline conditions, on the solubilities of compounds of Pu and of the neutron absorber elements Al(III), B as boric acid and borates, Cd(II), Cr(III) and (VI), Fe(III), Mn(IV), Ni(II), and U(VI). The solubility of Pu (as $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ above pH ~1) is highest at low pH, at a minimum around pH 10 – 13, and rises steeply above that pH because of hydroxide complexation. Ions of other metallic elements (i.e., Al(III), Cd(II), Cr(III), Fe(III), Ni(II), and U(VI)) have similar amphoteric behavior (i.e., higher solubilities at low and high pH than at intermediate pH) with lowest solubilities at intermediate to mildly alkaline pH values. In contrast, MnO_2 solubility is low and relatively unaffected by pH while Cr(VI) salts, sodium dichromate, $\text{Cr}_2\text{O}_7^{2-}$, and sodium chromate, CrO_4^{2-} , at low and high pH, respectively, and B, as boric acid and sodium borate salts at low and high pH, have relatively high molar solubilities.

For simplicity, other soluble sodium salts (e.g., nitrate, nitrite) are not shown in Figure 8. Similarly, this plot does not detail solubility behaviors of other solid phases found in the tank wastes such as the transition metal spinels (Fe_3O_4 , FeCr_2O_4 , Mn_3O_4 , Fe_2MnO_4) and mixed-element compounds, including the sodium aluminosilicates (e.g., cancrinite, sodalite, and albite), which also may be present in sludge.

Because iron is an abundant and effective neutron absorber, its parallel solubility dependency with that of Pu is important in criticality safety because pH swings will affect the solubilities of these two elements similarly and thus cause them to go together into the solution or solid phases.

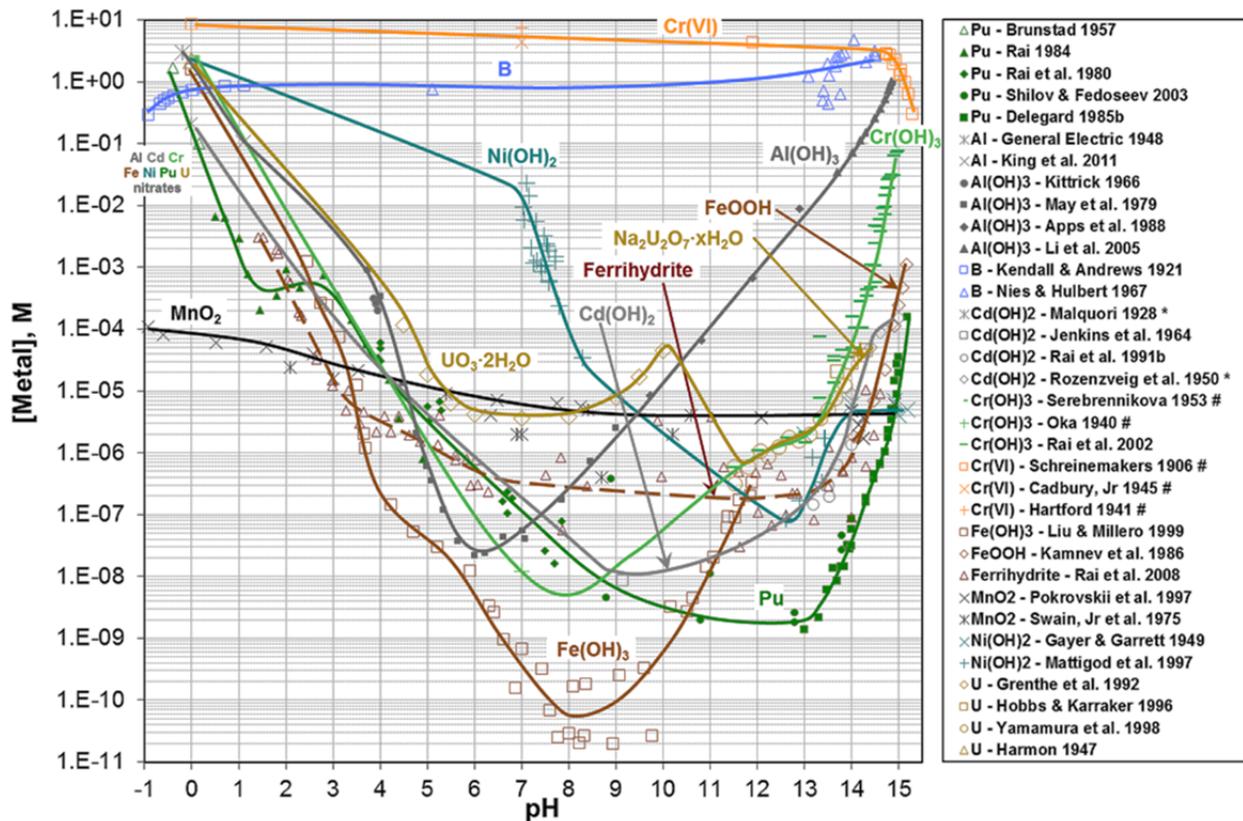


Figure 8. Solubilities of Pu and Absorber Element Compounds as a Function of pH (right panel: bibliographic information is found in Delegard and Jones (2015))

The effects of carbonate and bicarbonate on $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ solubility are large and illustrative of the influence of hydrolysis, i.e., interaction with hydroxide ion, as hydroxide concentrations increases. As shown in Figure 9, Pu solution concentration increases with the square of (bi)carbonate concentration, with the solubility being about a factor of 200 greater in bicarbonate (HCO_3^- ; pH 9 – 10) than in carbonate (CO_3^{2-} ; pH 12 and greater) at similar (bi)carbonate concentrations. The dissolved carbonate-complexed Pu species are anionic and species such as $[\text{Pu}(\text{OH})_4(\text{CO}_3)_2]^{4-}$ have been postulated based on the solubility dependence on the square of (bi)carbonate concentration. The Pu concentrations found in actual Hanford tank-waste solution as functions of carbonate concentration are consistent with laboratory findings (see red circle symbols in Figure 9).

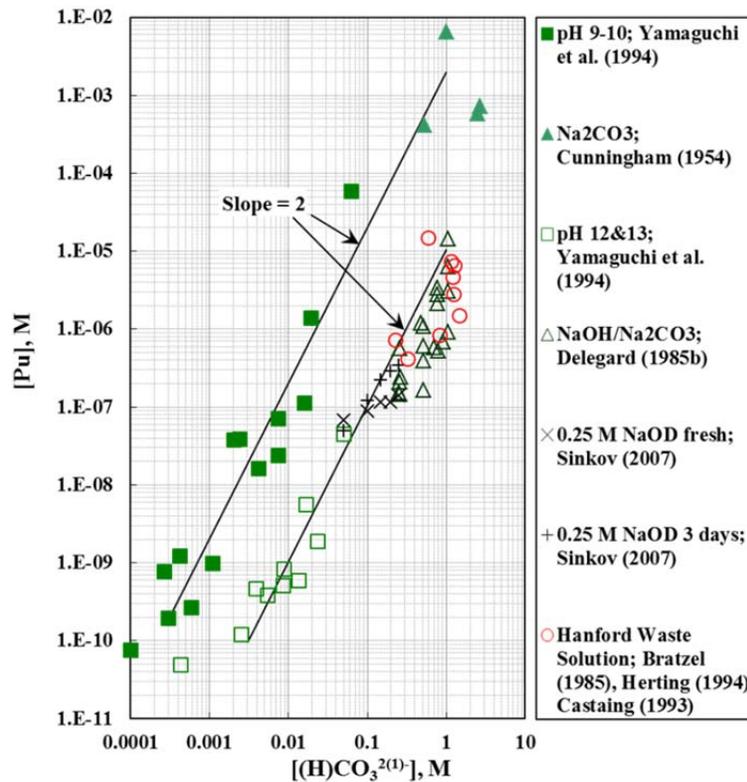


Figure 9. Pu Concentrations in Carbonate Solutions. Upper curve is for bicarbonate at pH 9-10; lower curve is for carbonate at pH 12 and higher. (bibliographic information is found in Delegard and Jones (2015))

While carbonate increases Pu solubility, the effect is smaller at higher pH due to competition with hydrolysis. Thus, Pu concentrations in bicarbonate-free pH 9 to 10 solution are about 10^{-10} M to 5×10^{-9} M (Figure 9 and Figure 8, respectively) whereas if such solutions are made 1 M in bicarbonate, Pu solubility grows to $\sim 2 \times 10^{-3}$ M (Figure 9), an increase in solubility by a factor of $\sim 10^6$. In highly alkaline solution (i.e., $\text{pH} \geq 12$) containing 1 M Na_2CO_3 , Pu concentrations are 10^{-6} to 10^{-5} M (Figure 9) compared with $\sim 10^{-6}$ M in 5 M NaOH, $\sim 10^{-7}$ M in 1 M NaOH, and $\sim 2 \times 10^{-9}$ M in pH 12 solution under non-oxidizing conditions in the absence of carbonate (Figure 7 and Figure 8). Although the relative impact of carbonate on Pu solubility decreases at molar hydroxide concentration, up to ten-fold increase in Pu concentration still can be attained in 3 to 5 M NaOH in the presence of 1 M carbonate.

4.3 Pu-Bearing Solid Phases in Hanford Tank Waste

Pu has been introduced into Hanford Site tank waste by a variety of vectors—coprecipitated with bulk polyvalent metal ions in alkaline solution, metathesized to hydrated Pu(IV) oxide from precursor Pu process solid phases as discrete Pu oxides from Pu recovery or fuel dissolution, or even Pu metal particles from losses in processing of burnt Pu metal buttons. The genesis of the Pu-bearing solid phases is examined in the following report section with most information found in the prior review by Delegard and Jones (2015) and references therein.

The following report section examines the genesis of the Pu-bearing solid phases.

4.3.1 Pu Solids from Precipitation Directly from Solution

The solid phase found in nearly every laboratory study of Pu solubility in alkaline solution is hydrated Pu(IV) oxide, $\text{PuO}_2 \cdot x\text{H}_2\text{O}$. Even with Pu(VI), the sodium-Pu(VI) salts that precipitate when acidic Pu(VI) nitrate is added to NaOH solution gradually alter by radiolytic processes to form hydrated Pu(IV) oxide. Only in the cases of Pu(IV) in the presence of alkaline silicate or phosphate do phases other than $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ form in alkaline solution. In these instances, Pu silicate and Pu phosphate solids form, whose silicate and phosphate complements decrease with increasing NaOH concentration (Krot et al. 1998; Yusov et al. 2000). For all other anions investigated in Pu precipitation tests in alkaline solution (e.g., nitrate, nitrite, carbonate, etc., as listed previously), the sole solid phase observed is $\text{PuO}_2 \cdot x\text{H}_2\text{O}$.

The water content of separated solid $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ is 1.6 to 2.8 moles, depending on the relative humidity. The x-ray diffraction (XRD) peaks for $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ are broad and occur in locations corresponding to those of refractory PuO_2 . The peak broadness is attributed to small (2 – 5 nm) crystallite size. These exceedingly small particle sizes are of similar dimension to those of Fe(III) hydroxide (2 – 3 nm) and sodium diuranate ($\text{Na}_2\text{U}_2\text{O}_7$; 3 – 4 nm) precipitated under alkaline precipitation conditions. This similarity in particle sizes is important in criticality safety because it means hydrodynamic actions (e.g., sluicing, pumping, shearing, sedimentation) will not physically separate the Pu particles from those of the important Fe and U neutron absorbers.

4.3.2 Pu in Coprecipitation

In general, however, Pu entered the alkaline Hanford tank-waste system, not as a separate pure acidic nitrate stream, but rather as a trace dissolved constituent within acidic process wastes containing much larger concentrations of Fe, Cr, Ni, Al, U, Bi, lanthanides (e.g., lanthanum, La), and other metal ions in nitric acid. These nitrate-dominated solutions contained generally lower associated concentrations of phosphate, sulfate, fluoride, chloride, and organic agents (e.g., oxalate, citrate, EDTA) from the various processes practiced at Hanford and from impurities in process chemicals and in raw water. The acidic process waste solutions were made alkaline using NaOH and sometimes sodium carbonate (Na_2CO_3) prior to their discharge to the mild-steel lined underground waste storage tanks. As a consequence of the resulting acid-base reactions, the bulk polyvalent metals precipitated as their hydroxides or hydrated oxides, carrying the trace Pu within their poorly crystallized solids by coprecipitation. The low-solubility solid materials arising from the precipitation of the polyvalent metal ions in the Hanford waste tanks is called ‘sludge.’¹

Plutonium coprecipitates with the (hydr)oxide sludge phases formed by making acidic polyvalent metal ion solutions alkaline. The polyvalent ions effective for coprecipitating Pu include Bi(III), Co(III), Cr(III), Fe(III), La(III) and other lanthanides, Mn(IV), U(VI), and Zr(IV). The very low water solubilities of several of these polyvalent metal ions are seen in Figure 8. For these listed metal ion (hydr) oxides, the Pu is atomically dispersed within the bulk sludge solid phases. Studies show that although Pu coprecipitates well with many metal ion (hydr)oxides, most importantly with the abundant and effective neutron

¹ Hanford tank wastes contain sludge, salt cake, and solution components. The major chemical present in the Hanford tank waste, after water, is the salt sodium nitrate, NaNO_3 . In fact, water and NaNO_3 constitute about 75 wt% of the tank waste. Other sodium salts (e.g., $\text{Na}_2\text{C}_2\text{O}_4$, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, $\text{NaAl}(\text{OH})_4$) and double salts (e.g., $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$, Na_3FSO_4 , $\text{NaAlCO}_3(\text{OH})_2$) also can be found as solid phases in the tank wastes. These materials constitute the salt cake portion of tank wastes. The third component of the tank waste is the supernatant and interstitial solutions containing NaOH, NaNO_3 , NaNO_2 , $\text{NaAl}(\text{OH})_4$, and other readily soluble sodium salts.

absorber Fe and its various (hydr)oxides, it does not coprecipitate with either Al(III) or Ni(II) hydroxides but instead forms a separate discernable hydrated Pu(IV) oxide solid phase in the midst of the bulk Al(III) or Ni(II) solid phases.

The uptake of Pu anions within the cage-like cancrinite and sodalite framework aluminosilicates formed by the presence of both dissolved Al and silicon in alkaline solution is unknown but unlikely given the larger size of plutonate anions (e.g., pentavalent $\text{PuO}_2(\text{OH})_4^{3-}$) compared with the chloride, carbonate, or nitrate anions ordinarily found enclathrated in these minerals. However, no experimental evidence was found to prove or disprove this hypothesis.

4.3.3 Intrinsic Pu Solids Expected to be Metathesized in Tank Wastes

Discrete particles of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ can form in alkaline Hanford tank waste by the hydrolysis of intrinsic Pu-bearing solid phases encountered in Pu processing operations. Thus, Pu precipitates from acid solution to form a solid compound with dibutyl phosphate (DBP), a hydrolysis and radiolysis product of the tributyl phosphate solvent used in the PUREX Process and in the Pu Reclamation Facility of the Pu Finishing Plant (PFP) on the Hanford Site. This Pu-DBP solid is a constituent of interfacial “crud” in the solvent extraction operations and is removed in solvent clean-up steps in PUREX and the PRF. The Pu-DBP compound hydrolyzes in alkaline solution to produce $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ and release the DBP as a water-soluble anion.

Pu fluoride salts such as PuF_4 and NaPuF_5 arise in Pu scrap recovery operations at the PFP, with PuF_4 also being a chemical intermediate in the preparation of Pu metal at PFP. These salts, too, are unstable to hydrolysis in the strong alkaline solution of the Hanford tank waste and will likewise form $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ with the fluoride being released as an anion into the tank waste. Pu oxalate, $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$, is another solid-phase intermediate in Pu metal production at the PFP and, if lost to the tank waste, will hydrolyze to form $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ and release oxalate.

4.3.4 Pu Oxide, Pu Metal, and Pu-Bearing Particles

Pu oxide, PuO_2 , was produced at the PFP and at PUREX, was a constituent of irradiated and mixed (U,Pu) oxide (MOX) fuel and PuO_2 fuel scrap reprocessed at the Hanford REDOX and PUREX Plants, and was a constituent of Pu process scrap handled at the PFP. Incomplete dissolution of the notoriously refractory PuO_2 and subsequent loss as a finely dispersed solid phase in these processes likely occurred in the Hanford Site tank wastes. Because of the stability of PuO_2 , little alteration of the solid phase aside from some minor changes in the crystal lattice by radiolysis is expected.

Pu metal scrap was processed for recovery at the PFP, with an initial step being burning of the metal to oxide, PuO_2 . However, sometimes the metal burning was incomplete and small particles of unburnt Pu metal persisted. The presence of what appears to be Pu metal particles is suspected in tank waste but remains unconfirmed. Other Pu-bearing phases also containing Bi and Bi plus P have been observed in some tank wastes as evidenced by electron microscopy and energy dispersive spectrometry (EDS). The process origins of the Pu-Bi and Pu-Bi-P phases are open to debate.

4.3.5 Pu Adsorption

Observations of Pu adsorption onto various ion-exchange and solid sorbents are summarized in the LANL work as seen in Figure 2 (from Table 8 of Marsh et al. (1995)). The highest uptakes were found for bone char and various titanates, but only for hydrothermally treated simulant waste solutions of very low hydroxide concentration (i.e., pH ~12). Observations of high Pu uptake onto engineered sodium titanates were also summarized by Delegard and Jones (2015). At 0.16 M NaOH for hydrothermally untreated simulant waste solution, Marsh and colleagues (1995) observed K_{ds} of ~5 mL/g for CS-100 resin; all other sorbents showed lower Pu uptake.

Often, however, findings in the technical literature on Pu sorption from alkaline solution are clouded because the tests were conducted at Pu spike concentrations exceeding solubility. Pu uptake from simulated and actual waste solution onto hematite and granulated activated carbon has been demonstrated, with Pu uptake onto Fe phases diminished by organic complexants. This finding likely is more a reflection of the affinity of the organic complexants for the solid substrate than for the dissolved Pu, given the lack of effect of organic complexants on Pu solubility in alkaline solution. Uptake of Pu(V) onto hydrated thorium oxide and lanthanum hydroxide and onto silicate minerals also has been observed.

4.3.6 Summary of Pu Solids Disposition in Hanford Tank Waste

Table 5 summarizes the dispositions of Pu solids in the Hanford tank wastes according to the process origins and interactions occurring upon making the waste alkaline for introduction to the underground storage tanks.

Table 5. Pu Solids Disposition in Alkaline Tank Wastes

Starting Pu Disposition	Other Agent	Pu Disposition in Waste with or after NaOH Treatment
With Anions		
Pu(NO ₃) ₄ solution	HNO ₃ only	PuO ₂ ·xH ₂ O; crystallites 0.002 to 0.005 μm
PuO ₂ (NO ₃) ₂ solution	HNO ₃ only	Eventually PuO ₂ ·xH ₂ O; crystallites ~0.01 μm
Pu(NO ₃) ₄ solution	Nitrate plus: nitrite, carbonate, sulfate, chromate, ferrocyanide, oxalate, glycolate, citrate, EDTA, or HEDTA	PuO ₂ ·xH ₂ O; crystallites 0.002 to 0.005 μm
	Nitrate plus phosphate	“Pu(PO ₄)O” where P:Pu≤0.15; unknown but small particle size
	Nitrate plus silicate	“Pu(SiO ₄)O” where Si:Pu = 0.3-1.8; unknown but small particle size
With Metal Ions		
Pu(NO ₃) ₄ solution	Dissolved nitrate salts of Bi(III), Co(III), Cr(III), Fe(III), La(III), U(VI), Zr(IV)	Coprecipitation
	Dissolved nitrate salts of Al(III), Ni(II)	Simultaneous precipitation; Pu exists separately as PuO ₂ ·xH ₂ O in nanometer-scale crystallites
	Dissolved Mn	Coprecipitation likely
	Dissolved nitrate salt of Cd(II)	Unknown
PuO ₂ (NO ₃) ₂ solution	Dissolved nitrate salts of Al(III), Cr(III), Fe(III)	Separate precipitation; Pu likely exists as nanometer- to sub-micron-scale crystallites
Pu Solid Compounds		
PuF ₄ solid and fluoride double salt solids	None	PuO ₂ ·xH ₂ O; likely μm-scale agglomerates of nm-scale small crystallites
Pu(C ₂ O ₄) ₂ ·6H ₂ O solid	None	
Pu in organic “cruds”	None	
PuO ₂ solid from scrap or fuels	None	PuO ₂ with little alteration; ~10-20 μm from oxalate; ~30 μm from burnt metal
Pu metal	None	Unknown (may or may not corrode)
Unknown	Unknown	Pu-Bi, Pu-Bi-P phases
Pu Adsorption		
Dissolved Pu	Various solids: ThO ₂ , La(OH) ₃ , calcium phosphate, Fe (hydr)oxides, titanates	Surface adsorption

4.4 Pu Concentrations in Hanford Tank-Waste Solutions, Sludge, and Salt Cake

The average Pu concentration in the Hanford tank waste system is about 0.004 g Pu/L, or about 1.66×10^{-5} M, based on 847-kg Pu inventory in the tank wastes and the 2.13×10^8 -liter tank waste volume (Delegard and Jones (2015) and references therein). The Pu concentrations observed in actual Hanford tank-waste solutions circa 1999 and shown in Figure 10 range from $\sim 10^{-9}$ to 10^{-5} M. As shown in Figure 9, Pu concentrations in several carbonate-bearing tank-waste solutions range from 4×10^{-7} to 1.3×10^{-5} M and thus are at the upper end of the concentrations reported in Figure 10 for tank-waste solutions.

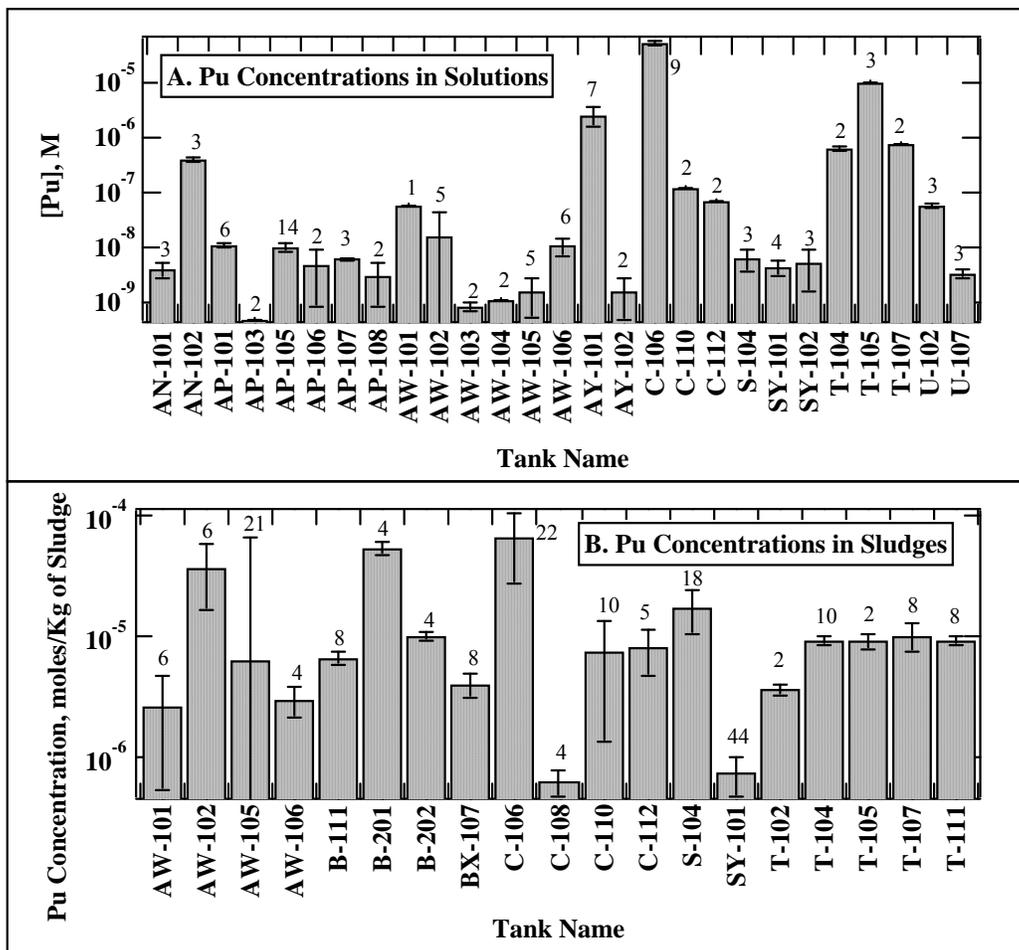


Figure 10. Hanford Tank-Waste Solution and Sludge Pu Concentrations (Barney and Delegard 1999) (error range and numbers of analyses shown for each bar)

The preference of Pu to report to low-solubility solid-phase constituents is indicated by Pu concentrations ranging from $\sim 10^{-6}$ to 10^{-4} moles per kilogram of dry sludge (Figure 10). Dry salt cake contains about 10^{-6} to 10^{-7} moles of Pu per kilogram, about a factor of 100 below the concentrations observed in dry sludge (Barney and Delegard 1999). Because Pu salts are unlikely to crystallize with the sodium salts that dominate salt cake, the Pu that is found in salt cake may reflect contamination of the salt cake by sludge particles.

Most, but not all, of the observed Pu concentrations in tank-waste solution are below the ICD-30 limit of 3×10^{-5} Ci ^{239}Pu /liter ($\sim 2.15 \times 10^{-6}$ M Pu) for LAWPS feed input. However, oxidative leaching of tank-waste sludge using permanganate has the potential to deliver higher Pu concentrations to the solution phase due to the greater availability of Pu in the sludge and the higher solubilities of the Pu(V) and Pu(VI) oxidation states attainable using permanganate. Aeration also could favor the more soluble Pu(V) over Pu(IV). Similarly, higher carbonate, and especially higher bicarbonate concentrations (at pH values less than 12), can potentially leach Pu from sludge and attain much greater Pu concentrations in solution.

The Tank Waste Information Network System (TWINS)¹ database was queried on August 16, 2016 for waste compositions in Hanford tanks that contain primarily aqueous solutions (AN, AP, AW, AY, AZ, S, and SY tank farms). The composition query was limited to total organic carbon (TOC), total inorganic carbon (TIC), Na^+ , OH^- , Pu, and $^{239,240}\text{Pu}$. Although 419 Pu concentration values were obtained, not all datasets were complete; for example, a particular dataset might have Pu, TOC, OH^- , and Na^+ concentration values but have no TIC value.

These data were downloaded as a Microsoft Excel file and organized according to tanks, specific sampling event, and segment. Samples that included $^{239,240}\text{Pu}$ as part of the analytical suite and that were reported in terms of volume (e.g., $\mu\text{Ci/mL}$, $\mu\text{g/mL}$, M) were further evaluated. For example, for $^{239,240}\text{Pu}$ values reported in terms of microcuries per milliliter, conversion to units of molarity proceeded according to the following equation:

$$\frac{A_{\text{Pu}}}{\text{SpA} \times \text{AW}_{\text{Pu}} \times 1000} = M_{\text{Pu}}$$

where A_{Pu} = reported activity concentration of $^{239,240}\text{Pu}$, $\mu\text{Ci/mL}$.

SpA = specific activity of $^{239,240}\text{Pu}$, 0.071542 $\mu\text{Ci/g}$, calculated from the weighted projected isotopic composition of 93.9 wt% ^{239}Pu and 5.8 wt% ^{240}Pu (Footnote *a* of Table 1).

AW_{Pu} = Pu atomic weight, 239.11, for the Pu isotopic composition given in Footnote *a* of Table 1.

1000 = conversion factor from μmoles to mmoles .

The TOC sample concentrations were converted to terms of carbon molarity (dividing by mass factor 12 g/mole). The TIC sample concentrations were converted to terms of carbonate molarity (dividing by mass factor of 12 g/mole). For duplicate/replicate sample results, average values were reported.

The Pu concentrations found in actual tank-waste solutions ranged from $\sim 2 \times 10^{-10}$ M to $\sim 6 \times 10^{-5}$ M, comparable to those found in the ~ 1999 survey (Figure 10). Only eleven of the 419 observed Pu concentrations exceeded the $\sim 2 \times 10^{-6}$ M threshold of criticality concern promulgated in ICD-30.

Plots of Pu concentrations as a function of OH^- concentration, abstracted from TWINS, then were compared with Pu compound solubilities in the “pure” NaOH system as derived in laboratory tests. This comparison, Figure 11, indicates undersaturation in Pu concentration by a factor of 10 to 20 at NaOH concentrations greater than about 1 M NaOH for a majority of the data, with a majority of points of oversaturation being below 1 M NaOH. Whereas undersaturation is plausible because of insufficiency of

¹ TWINS; <https://twins.labworks.org/twinsdata/Forms/About.aspx>.

Pu or its coprecipitation or sorption, oversaturation indicates that something besides OH^- complexation is responsible for the observed enhanced Pu concentration.

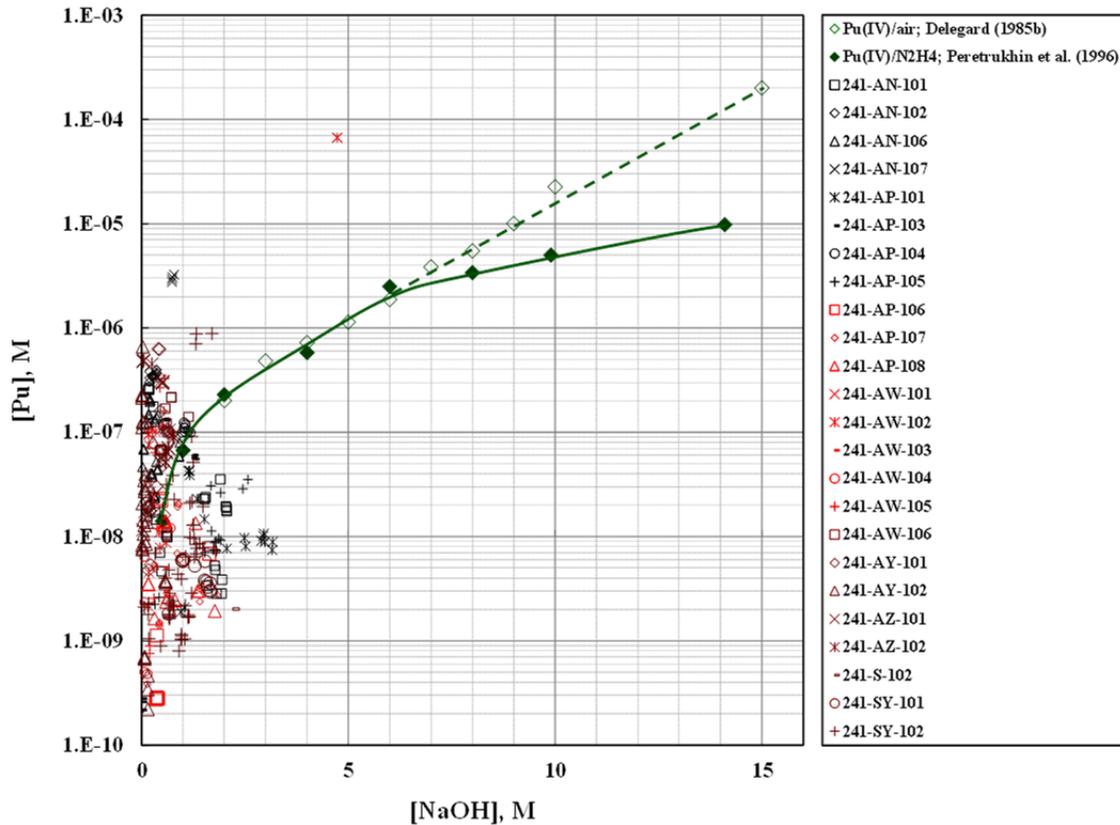


Figure 11. Pu Compound Solubilities in Laboratory Tests with “Pure” NaOH Solution and Pu Concentrations in Actual Tank Wastes from TWINS Data as Functions of NaOH Concentration

Therefore, the observed tank-waste Pu concentrations were plotted versus the carbonate concentrations and compared with observations from laboratory tests and prior tank-waste measurements (i.e., those data shown in Figure 9) to see whether carbonate complexation were responsible for the Pu concentrations that are higher than can be explained by hydroxide complexation in the tank-waste solutions. The comparison plot, Figure 12, shows that the maximum Pu concentrations in actual waste (which have $\text{pH} \geq 12$) generally follow the carbonate line, but most concentrations are below that line, indicating undersaturation with respect to carbonate complexation. The concentrations below the saturation values can be explained as instances where Pu is either unavailable, is sorbed, or is coprecipitated with Fe hydroxides or other constituents, such as hydroxides of transition metals and lanthanides, which are not dissolved by carbonate. Only two points of >400 deviate more than a factor of five above the predicted concentration.

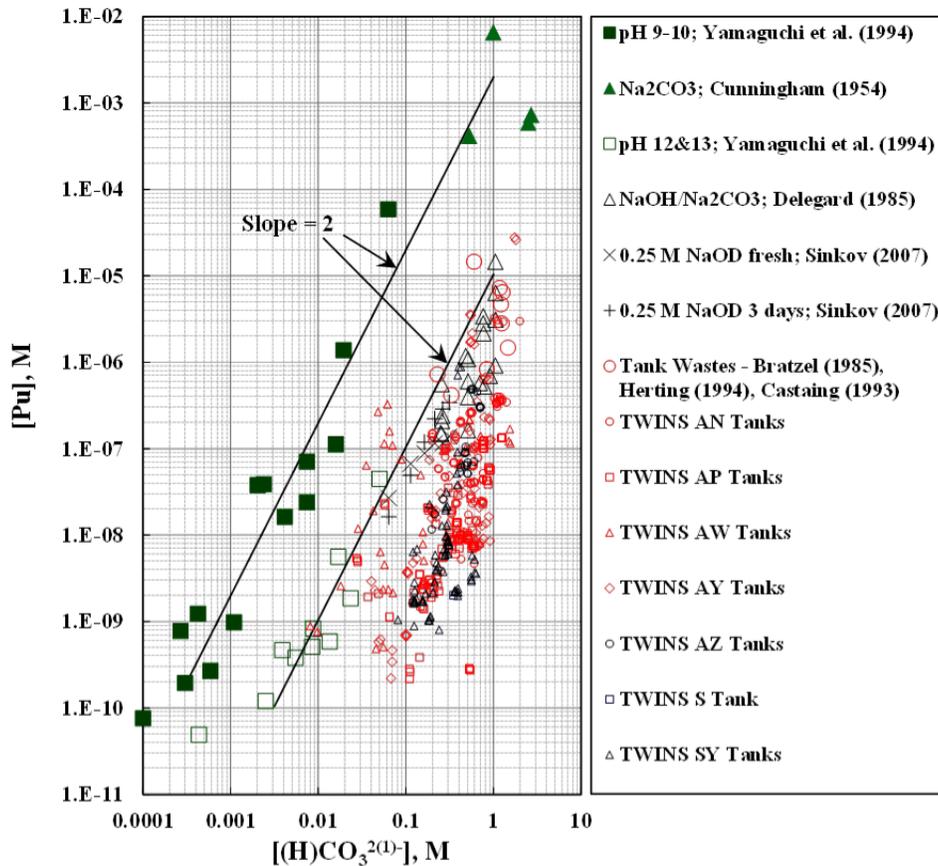


Figure 12. Pu Concentrations in Carbonate Solutions in Laboratory Tests, Prior Tank-Waste Measurements, and in Actual Tank Wastes from TWINS Data as Functions of Carbonate Concentration

Freer (2014) recognized the possibility of oxidative leaching and (bi)carbonate leaching of Pu from sludge solids in WTP operations; Delegard et al. (2015) examined the impacts these phenomena might have in separating Pu from neutron absorbers.

As shown in Figure 9, Pu compound solubility is strongly enhanced by the presence of carbonate at pH ≥ 12 and even more strongly enhanced by bicarbonate at pH 9 to 10. The extent of Pu leaching from solids that contain coprecipitated Pu depends on the susceptibility of the host solids to dissolving and releasing the contained Pu. Laboratory testing shows that Fe-bearing precipitates do not dissolve in (bi)carbonate and thus do not release their contained Pu while U-bearing solids dissolve in (bi)carbonate solution to release their Pu. Compounds of other absorbers that are effective in coprecipitating Pu but have low solubility in (bi)carbonate (e.g., Cr(III), Co, La, Mn, and Zr) will release little of their contained Pu. (Hydr)oxide compounds of Al and Ni do not coprecipitate Pu, and Pu leaching from Al solids by (bi)carbonate is known. Therefore, leaching of Pu from Ni solids by (bi)carbonate is also likely. Intrinsic Pu solids present in the waste, such as $\text{PuO}_2 \cdot x\text{H}_2\text{O}$, are expected to be susceptible to dissolution by (bi)carbonate, although rates likely will be low for high-fired PuO_2 .

Hydrated Pu oxide and the (hydr)oxide compounds of Al, Cd, Fe, and U, but not Mn(IV) or Ni, have higher solubility with increasing molar NaOH concentration and thus help retain the Pu/absorber ratio in solution. However, the Pu/absorber ratio may alter in oxidative Pu dissolution by permanganate. This

oxidative dissolution is enhanced by a factor of ~70 at 3 M NaOH when compared with 0.1 or 0.25 M NaOH. Even though increasing NaOH concentration increases oxidative leaching, increased permanganate concentration does not increase Pu dissolution. In any event, enhanced Pu dissolution can be mitigated by addition of chromium(III) nitrate to eliminate excess oxidant to form MnO_2 and thus remove ~95% of the solubilized Pu by coprecipitation; H_2O_2 (hydrogen peroxide) also eliminates excess permanganate and causes oxidized Pu to be carried by the MnO_2 which precipitates.

5.0 Potential Mechanisms for Pu Uptake and Retention onto sRF

The observations reported herein of Pu uptake and retention onto sRF are cause for criticality concern. Therefore, understanding the mechanisms responsible for this uptake and retention is key to devising methods to overcome the affinity of Pu for sRF.

The uptake and elution of Pu in sRF resin column testing has been considered in a recent paper study on processing effects that might influence interactions of Pu with neutron absorbers during routine and upset conditions at the WTP (Delegard et al. 2015). Using the findings from the Cs ion exchange studies onto sRF resin performed by Fiskum and colleagues (2009), that study found that the criticality potential in the eluate (and the loaded resin) would be mitigated by the co-elution (and co-location) of cationic neutron absorbers, primarily sodium, from the tank-waste feed. The Pu:absorber mass ratios in the eluate, in grams of Pu per kilogram of absorber, were: Cr – 0.7 (6.28), Fe – 0.5 (5.18), Mn – 2 (25.5), Ni – 0.8 (9.68), and Na – 0.0003 (2.47) (based on Tables 5.10 and 5.11 of Fiskum et al. (2009)), wherein the numbers in parentheses indicate the upper threshold values for Pu:absorber mass ratios based on Table 4-2 of Miles (2009). Uranium and particularly boron are also present in the eluate. These values show that all of the listed absorbers provide criticality safety factors of about ten and, for sodium, almost a factor of 10,000. However, if tank-waste feed solutions approach the ICD-30 limit of $\sim 2 \times 10^{-6}$ M Pu, nearly 500-times higher in Pu concentration than the 4.67×10^{-9} M Pu present in the tests reported by Fiskum and colleagues (2009), only sodium would provide sufficient intrinsic neutron absorption.

This section discusses potential mechanisms for Pu uptake onto the sRF resin.

5.1 Solid-Solution Separation

Because of the low solubilities of Pu phases in alkaline solution, a very plausible mechanism by which Pu could be retained on sRF resin is by filtration of low-solubility Pu particles within the resin bed. As noted by Losey (2016a) and shown in Figure 5, sub-micron particles exhibit increasing Pu retention as size decreases within ~ 450 - μm particle sphere sRF beds. It should be noted that intrinsic (or true) Pu particle colloids such as $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ need not be the species filtered; similarly sized particles that contain adsorbed or incorporated Pu can be retained just as well. These so-called pseudo colloids, which are Pu-borne within sub-micron particles largely composed of other materials, can migrate or be retained within geological media. Alternatively, attachment of intrinsic Pu colloids onto colloids of non-Pu materials also can occur. The behaviors of Pu intrinsic and pseudo colloids and of associated intrinsic and Pu-free colloids have been the subject of a number of studies surrounding nuclear waste repository performance (see, for example, Abdel-Fattah et al. (2013)).

The five column tests of sRF and RF resin performance enumerated at the beginning of this report (Fiskum et al. 2006a; Fiskum et al. 2009; Fiskum et al. 2006c; Hassan and Adu-Wusu 2003; Nash and Duignan 2010) were undertaken using feed solutions filtered using 0.1 to 0.45 μm pore-size media. However, the efficacy of filtration in removing Pu-bearing sub-micron particles could be called into question. The CUF to be used in actual waste processing in the LAWPS relies on a 0.1- μm sintered metal

filter medium, but the solid-solution separation will occur largely by depth filtration through the bulk sludge solids collecting on the CUF, not by the sintered metal medium itself.

5.2 Chemical Reduction via Chemical Reductants in the sRF

The Pu in the waste solutions for the five column tests could have been present in the feed solutions in their more soluble Pu(V) or Pu(VI) oxidation states. The dissolved Pu then could have been chemically reduced within the organic sRF resin to the much less soluble Pu(IV) oxidation state and then been captured or adsorbed as a solid or contact reduced in a process analogous to electrodeposition.

The ~9 to 13% Pu uptake shown in the tests using actual waste from tank AP-101 (Fiskum et al. 2006a) was greater than ~1.4% Pu uptake in subsequent tests on the same resin using waste from tank AN-102 (Fiskum et al. 2006c). The 0.5 M HNO₃ elution after the initial loading thus may have removed the chemically reducing impurities, suggesting that chemically reducing agents present on the sRF resin may be amenable to removal by washing or wet oxidation with HNO₃.

As shown in Figure 13, the feed solutions in each of the five enumerated tests contained Pu solution concentrations below or well below the solubilities indicated for Pu(IV) as driven by hydroxide complexation and well below those predicted for carbonate complexation (5×10^{-7} to 2×10^{-5} M) based on the solutions' 0.24 to 1.18 M carbonate concentrations. Thus, the Pu was not present in the more soluble Pu(V) or Pu(VI) oxidation states, and even was unsaturated with respect to Pu(IV). However, assignment of the dissolved Pu oxidation state to (IV) is inconsistent with what would be expected based on the solubility of the Pu(IV) chemical analog thorium(IV) in strong alkaline solution and the lack of amphoteric behavior for thorium(IV)— see (Ryan and Rai 1987). The solubility of amorphous thoria, ThO_{2(am)}, was measured to be near the detection limit at $\sim 10^{-10}$ to 10^{-9} M at pH 14 (equivalent to 1 M NaOH) in these tests. Based on the thorium findings, the projected solubility of PuO_{2(am)} as Pu(IV) dissolved species would be $\leq 2.3 \times 10^{-10}$ M at pH 14 (Ryan and Rai 1987), about a factor of 400 lower than observed (see Figure 13).

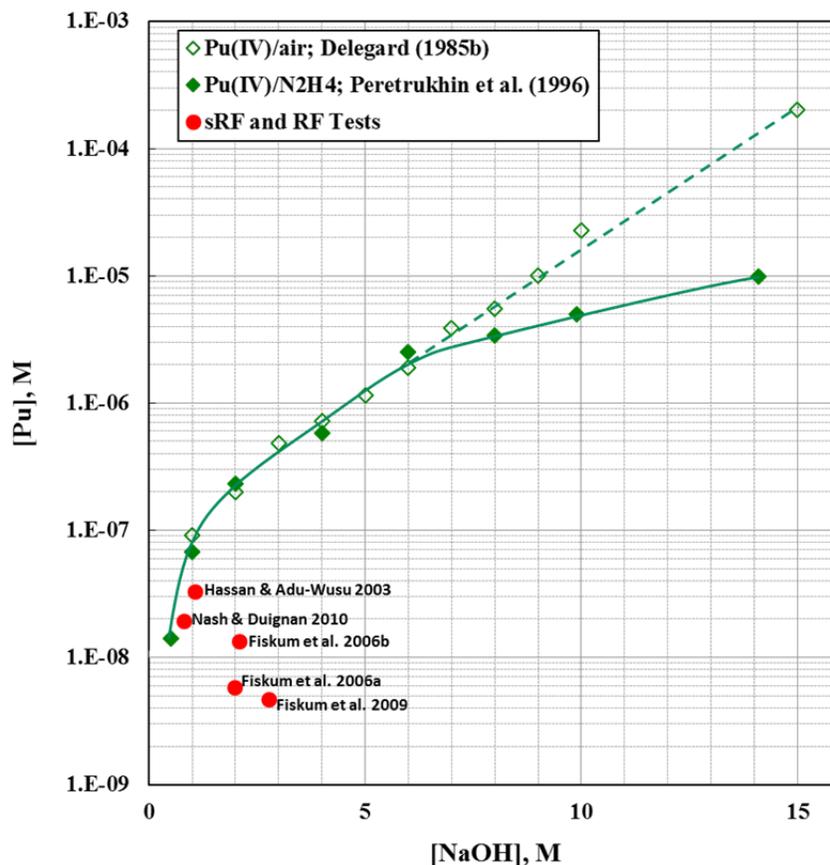


Figure 13. Pu Concentrations in sRF and RF Test Solutions (see Delegard and Jones (2015) for references cited in the legend)

Therefore, if the true solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ at 1 to 3 M NaOH were $\sim 10^{-10}$ M, and if the sRF resin contained a more potent reductant than hydrazine, reductive precipitation or deposition of the Pu could have occurred in the sRF resin column tests. Potent reductants used in tests of the solubilities of the $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ analogs $\text{UO}_2 \cdot x\text{H}_2\text{O}$ and $\text{NpO}_2 \cdot x\text{H}_2\text{O}$ include sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) and metallic zinc, Fe, Ni, and Pb (Rai and Ryan (1985); Ryan and Rai (1983), respectively). Without reductants, Pu concentrations on the order of 10^{-10} to 10^{-9} M were observed in tests at pH ~ 13 (Neck et al. 2007), and $\sim 1.5 \times 10^{-9}$ M Pu was observed at 0.1 M NaOH (pH 13) with and without 1 M NaNO_3 / 1 M NaNO_2 (Delegard 2006). The effects of reductants other than hydrazine on Pu solution concentration in the actual waste solutions containing ~ 1 to 3 M NaOH, which is the approximate concentration range of the five sRF and RF column ion-exchange tests (Figure 13), remain to be determined.

5.3 Chemical Reduction via Resin Radiolysis Reactions

The creation of chemically reducing conditions also could occur within the sRF resin bed by radiolytic processes. It is known that organic molecules (e.g., EDTA, formate, various alcohols) in alkaline solution can scavenge strongly oxidizing water radiolysis products such as the OH radical and its deprotonation product O^- , leaving the countering radiolytic water reduction products such as the hydrated electron, H_2O^- , free to act (Pikaev et al. 1996). Therefore, the interaction of water radiolysis products with the organic structures in the sRF could lead to chemical reduction of Pu(V) to less-soluble Pu(IV). However,

$\text{PuO}_2 \cdot x\text{H}_2\text{O}$ solubility in 1 to 4 M NaOH solution was not altered in the presence of 0.05 M EDTA, nor in the presence of 0.1 M HEDTA (N-2-hydroxyethyl ethylenediaminetriacetate), 0.1 M glycolate, or 0.05 M citrate (Delegard and Gallagher 1983). Nevertheless, the specific concentration or density of organic material in the sRF is greater than that available in the earlier solubility testing and may exert a greater impact in creation of reducing agents by radiolysis.

5.4 Pu Precipitation as a Silicate

Krot et al. (1998) and Yusov et al. (2000) observed the formation of Pu(IV)-silicate solids from alkaline solution containing dissolved silicate. The infrared spectra of the solid phase indicate the presence of silicate, while the solids have almost no XRD reflections to indicate the presence of PuO_2 crystallites. The relative quantity of silicate reporting to the solid phase decreases with increasing NaOH concentration, with the Si:Pu mole ratios decreasing from 1.38 to 0.88 as NaOH concentration increases from 0.2 to 1 M at room temperature and to 0.30 in 7 M NaOH at 100°C. The stability of the Pu(IV) silicate was confirmed by exposing pre-formed $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ to alkaline 0.05 M Na_2SiO_3 ; the solid was found to metathesize to form the mixed Pu(IV)-silicate solid. As noted by Yusov and colleagues (2000), page 159, “It follows from the above data that pure $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ cannot exist in alkaline waste containing substantial amounts of silicate.”

The formation of a Pu(IV)-silicate phase as observed by Yusov and colleagues (2000) under these alkaline conditions indicates that the solubility-controlling solid is a Pu(IV) silicate and not $\text{PuO}_2 \cdot x\text{H}_2\text{O}$. The Pu concentration in the solution in equilibrium with the Pu(IV) silicate therefore will be lower than that for $\text{PuO}_2 \cdot x\text{H}_2\text{O}$. Thus, the Pu retention observed on sRF could be a consequence of its lower solubility (and lower Pu concentration in solution) in the presence of the Pu(IV) silicate arising from the glass columns in which the tests were performed.

The enclathration of Pu within the cage structure of sodium aluminosilicate (NAS) phases such as sodalite or cancrinite may be dismissed based on the vastly different sizes of the anions normally found in sodalite and cancrinite (e.g., chloride, nitrate, carbonate, chromate) and the Pu anions such as pentavalent $\text{PuO}_2(\text{OH})_4^-$ or perhaps tetravalent $\text{Pu}(\text{OH})_5^-$. However, incorporation of U with NAS, or at least their common precipitation, has been observed as scale deposition within evaporator operations at SRS. Therefore, further NAS precipitation occasioned by the presence of additional dissolved silica by glass leaching may remove Pu from solution through a coprecipitation or simultaneous precipitation mechanism. Cancrinite and related phases were identified in the solids separated from the feed materials used in the column testing reported by Fiskum et al. (2009). Therefore, the solution used in at least this test of sRF resin was already saturated with respect to such solids and had more than adequate Al (0.27 M; Table 1) present in solution to react with silicate leached from glass.

In Table 5.10 of their work, Fiskum et al. (2009) notes that the silicon concentration in the composite REDOX sludge digestate and saltcake solution column test feed was 3.82×10^{-3} M, a factor of 3.4 higher than the effluent at 1.12×10^{-3} M. This suggests that silicate may have precipitated within the column, even though the Si concentrations in the column did not reflect this.

5.5 Pu Sorption onto Resorcinol and Catechol Functional Groups in the sRF Resin

The sRF resin is prepared using resorcinol, 1,3-benzenediol, the meta isomer of dihydroxybenzene. However, dihydroxybenzene also exists in two other isomeric forms—the ortho isomer 1,2-benzenediol (catechol) and the para isomer 1,4-benzenediol (hydroquinone), as shown in Figure 14. As discussed below, catechol exists as a significant impurity in commercial resorcinol.

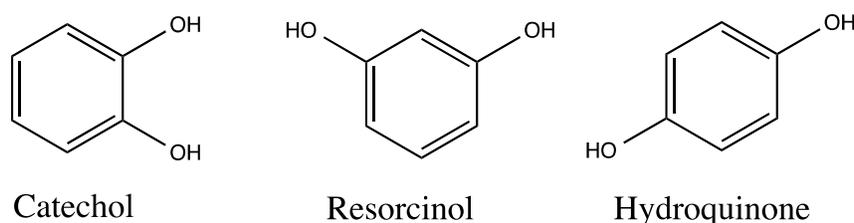


Figure 14. Chemical Structures of 1,2-Benzenediol (Catechol), 1,3-Benzenediol (Resorcinol), and 1,4-Benzenediol (Hydroquinone)

Hydroquinone and catechol are easily and reversibly oxidized under mild conditions, with oxidation favored by formation of resonance-stabilized semiquinone and quinone (Figure 15 and Figure 16). Oxidation of resorcinol is less favorable than that of hydroquinone and catechol because the resulting meta semiquinone radical does not undergo resonance stabilization. As a result, resorcinol is less prone to oxidation and its chemical properties remain similar to those of phenol.

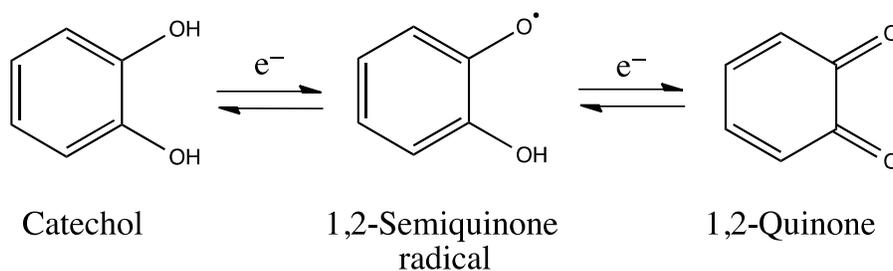


Figure 15. Redox Cycle for Catechol

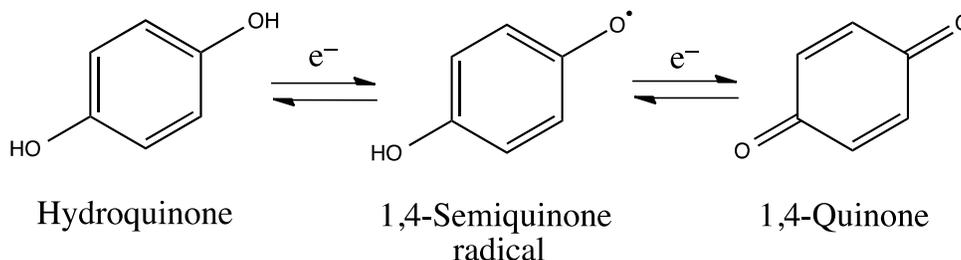


Figure 16. Redox Cycle for Hydroquinone

All three isomers can bind metal ions through deprotonation of their respective $-OH$ functional groups. Within the sRF resin, the $-OH$ functional groups of resorcinol are deprotonated in strongly alkaline solution to form the $-O^-$ anionic groups that are responsible for the strong attraction of cationic Cs^+ in ion

exchange that makes sRF useful in removing ^{137}Cs from the alkaline waste solutions. Similarly, other metal ions can interact through σ -bonding to the oxygen atoms of the dihydroxybenzenes.

While complexes of transition metal ions with catechol and hydroquinone derivatives have been studied for several decades (see, for instance, Pierpont and Lange (1994) and references therein), complexation properties of resorcinol have been studied only rarely. This report reviews the available relevant literature on the coordination of actinides or their analogs by resorcinol and catechol is reviewed in this report. Hydroquinone ligands are not considered herein, based on the information that commercial resorcinol contains catechol and not hydroquinone as a chief impurity.¹

The uptake of Pu by the sRF and RF resins and inefficient acid stripping can potentially be attributed to Pu complexation by alkoxide groups of resorcinol as well as by the impurity catechol within the resin matrix. In addition, incidental neighboring alkoxide groups within the RF polymers also may provide cavity-like cages that would satisfy the electronic and steric coordination requirements of the dissolved Pu ion. Furthermore, while resorcinol is a monodentate ligand (meaning that it can only coordinate through a single $-\text{O}^-$ moiety), catechol is a bidentate chelating agent whose vicinal $-\text{O}^-$ groups are well suited for Pu ligation. Catechol has known affinity for hard metal ions that exhibit a high charge-to-ionic-radius ratio, such as trivalent and tetravalent actinides. In particular, catechol has long served as a scaffold for the design of selective sequestration agents for Pu(IV) and Am(III) (Gorden et al. 2003). Solid compounds with $[\text{M}(\text{IV})\cdot\text{Catechol}_4]^{4-}$ composition, where M(IV) is U, Th, Ce, or Hf, have been obtained by alkaline-side precipitation (Sofen et al. 1978; Sofen et al. 1979).

Formation of the similar Pu(IV) tetrakis(catecholate) complex in alkaline solutions is supported by electrochemical studies (Kappel et al. 1985). These have found that the Pu(IV)-catechol complex undergoes a quasi-reversible one-electron reduction in alkaline solution containing 0.1 M KOH in the presence of excess catechol. The associated very large negative shift (-1.82 V) of the standard Pu(IV)/Pu(III) redox potential in presence of catechol indicates the strength of the complexation reaction. It was suggested that, like other tetravalent metal ions, Pu(IV) forms a tetrakis(catecholate) complex while the net stoichiometry of the Pu(III)-catechol complex is 1:2.5, suggesting mixture of 1:2 and 1:3 complexes (Raymond et al. 1984). These results are consistent with alkaline-side solvent extraction of americium(III) and lanthanide(III) ions from 0.05 to 1.5 M K_2CO_3 at pH 11 to 13.5 solution using catechol-based extractants (Karalova et al. 1988). The latter authors note that the extraction process is driven by the formation of a stable metal catechol chelate compound in the organic phase and requires dissociation of the (stable) aqueous carbonate complex.

Due to the similar complexation behavior of Pu(IV) and thorium(IV) and despite their different ionic sizes, thorium(IV) has often served as a convenient model for Pu(IV) in biological and other systems (Gorden et al. 2003). Research shows that Th(IV) forms strong complexes with resorcinol (Thakur et al. 2006). In solutions with pH above 3, mixed hydroxo-resorcinol complexes with proposed $[\text{Th}\cdot\text{resorcinol}_3\cdot\text{OH}]^{3-}$ and $[\text{Th}\cdot\text{resorcinol}_4\cdot(\text{OH})_2]^{6-}$ compositions are formed; the latter is the dominant soluble Th species in solution at pH 5 and above. Both complexes exhibit high stability constants with the respective logarithmic values of 46.46 and 59.64. Interestingly, under the same conditions, catechol

¹ Resorcinol is available in technical grade and USP grade with a purity of a minimum of 99.5% and contains phenol (maximum 1%), catechol, 3-mercaptophenol, ortho- and meta-cresol (maximum 0.1% each) impurities—(K. W. Schmiedel and D. Decker, "Resorcinol," *Ullmann's Encyclopedia of Industrial Chemistry* (Weinheim, Germany: Wiley-VCH Verlagsgesellschaft, 2000 (Online: 2011)).

formed only one observed and significantly weaker complex, $[\text{Th}\cdot\text{catechol}\cdot\text{OH}]^+$. Similar reactivity can be anticipated for Pu(IV), and taking into account comparable stability of the mixed hydroxo-carbonate $[\text{Pu}\cdot(\text{CO}_3)_2\cdot(\text{OH})_4]^{4-}$ and $[\text{Pu}\cdot(\text{CO}_3)_2\cdot(\text{OH})_2]^{2-}$ complexes with the respective stability constants of 46.4 (Yamaguchi et al. 1994) and 44.8 (Rai et al. 1999) on the logarithmic scale, exchange of the carbonate ligand for the resorcinol alkoxide groups in RF resin is reasonable.

Agarwal and Mehrotra (1962) investigated coordination reactions of thorium(IV) with catechol in aqueous solution by potentiometric titration. Their research suggested formation of a single $[\text{Th}\cdot\text{catechol}]^{2+}$ complex at acidic pH and the 1:1 Th:catechol stoichiometry is consistent with other findings (Thakur et al. 2006), as described above. On the alkaline side, formation of the higher order Th-catechol complexes was proposed, however extensive hydrolysis of Th(IV) precluded determination of the exact stoichiometry. Another study demonstrated that in the pH range of 2 to 8, catechol-functionalized silica gel exhibits rather weak affinity for Th(IV) extracting only about 60% but shows quantitative extraction of U(VI), which can be exploited to effectively separate U(VI) from Th(IV) (Metilda et al. 2005). Another tetravalent metal, Zr(IV), which exhibits hydrolysis and coordination behavior similar to that of Pu(IV), forms strong complexes with catechol of type $[\text{M(IV)}\cdot\text{catechol}_3]^{2-}$ and $[\text{M(IV)}\cdot\text{OH}\cdot\text{catechol}_2]$ at pH 5 and above (Kapoor and Mehrotra 1957a). Such complexes are prominent in 2 M KOH solution (Kapoor and Mehrotra 1957b). Interestingly, these studies suggest that at an acidic pH of 1.5 to 5, zirconyl forms 1:1 complex with protonated catechol. Formation of the similar Pu(IV) complex with protonated catechol may explain Pu retention by the sRF resin during stripping by 0.5 M HNO_3 .

For the above reasons, the formation of Pu complexes with resorcinol and with impurity catechol in sRF resin under alkaline conditions is plausible. The hypothesis of Pu complex formation with resorcinol is additionally supported by studies which have explored lanthanide retention and separation using phenolic ion-exchange resins, as Wiley (1976b, a, 1978) noted.

The behaviors of lanthanide ions are often used to predict coordination behavior of actinides, particularly those that are trivalent. Because of the ion size similarity between trivalent lanthanides and actinides, lanthanides serve as useful models for trivalent actinide behaviors with catechol-like ligands in particular, for which the metal charge-to-ionic-radius ratio is the main factor determining the strength of the complex. Shady and colleagues (2011) investigated the interaction of light lanthanides to RF resin converted to the Na^+ form by contact with NaCl and found that the affinity increases in the order samarium > cerium > neodymium > lanthanum, generally correlating with a decrease in the ionic radius of the dehydrated metal ion. The observed higher affinity of the RF resin for cerium over neodymium, which has a smaller dehydrated ion radius than cerium, was attributed to the presence and strong complexation of the cerium ion in oxidation state +4 by the RF resin. That work also noted that retention of lanthanides by the RF resin increases as the solution pH rises from 1 to 7.5; this increase was the most pronounced for samarium.

In a different study, (Draye et al. 2000) investigated catechol and resorcinol resins synthesized with and without 8-hydroxyquinoline for the separation of europium from lanthanum. Catechol and resorcinol resins in their protonated forms were found to be inefficient for lanthanide sorption, having to be treated with 1 M NaOH to convert them to the Na^+ form. Both catechol and RF resins exhibited quantitative sorption of Eu and lanthanum under the study conditions at pH of 4 and no separation selectivity was observed.

Taken together, this information supports the hypothesis that Pu may be retained on the sRF resin by surface complexation to form mixed $[\text{Pu}\cdot\text{resorcinol}_n\cdot(\text{OH})_m]^{4-2n-m}$ and/or $[\text{Pu}\cdot\text{catechol}_n\cdot(\text{OH})_m]^{4-2n-m}$ complexes.

5.6 Pu Entrapment by Resin Channel Shrinkage and Collapse

Plutonium is retained in the sRF and RF resin even after elution, possibly due to physical entrapment of the Pu within the pores of the resin. When the Na^+ form of the sRF resin, with nominal 450- μm bead size, converts to the H^+ form during elution using 0.5 M HNO_3 , it attains nominal 400- μm bead size. However, while this is an appealing argument, it does not reflect the behavior of Cs^+ upon elution, nor does it reflect the fact that Pu solubility is much greater in 0.5 M HNO_3 than it is in NaOH solution.

6.0 Proposed Experimental Plan

The foregoing narrative has outlined observations of Pu uptake and retention onto sRF from alkaline radioactive waste solution in column-type ion-exchange tests conducted at PNNL and at SRNL and the implications of such retention in nuclear criticality safety. This report has provided further examination of Pu uptake from alkaline solution onto RF and other organic and inorganic ion exchangers and sorbents and outlined the chemistry of Pu in alkaline media. Finally, this account has posited potential mechanisms by which the Pu might have been retained on the sRF. Although the discussion has advanced several potential means by which the Pu might have been sorbed and retained, the collected findings from the experimental studies and investigation of the technical literature do not point unambiguously nor with certainty to a mechanism for the observed Pu uptake and retention.

In the absence of a known reason for the observed Pu uptake and retention, PNNL proposes a program of laboratory experimentation to help identify the operant mechanism(s) and thus guide a technically defensible path forward to resolve the underlying criticality safety issue. The following proposed laboratory test program is arranged to conduct simpler and less costly batch tests initially, and then use the results from these early tests to inform the necessity and guide the extent of any further experimentation such as column testing. The variety of potential means by which Pu may become associated with, and retained on, the sRF and sRF columns necessitates a broad variety of simple tests for these initial laboratory efforts. This section of the report describes the proposed initial test approach is described in.

6.1 Preparation of Pu-Bearing Alkaline Solutions

Key to the experimental program is the preparation of Pu solutions of known oxidation state in alkaline solution. Guidance on how to prepare such solutions is available based on careful experimental methods developed and used to prepare Pu(V) and Pu(VI) solutions in NaOH and NaOH/Na₂CO₃ matrices (Sinkov 2007).

All Pu-bearing solutions will begin with acidic Pu(IV) nitrate that has been purified by anion exchange and then stored in ~3 M HNO₃ solution.

A Pu(V) stock solution in concentrated NaOH may be prepared by adding known amounts of the Pu(IV) acidic stock solution to an excess of ~15 M of NaOH. With time (20+ days) and stirring, a portion of the initial PuO₂·xH₂O that precipitates immediately oxidatively dissolves and Pu(V) solution arises, apparently by radiolysis, in association with PuO₂·xH₂O solids. The solution may be separated from the solid using a NaOH-resistant filter (e.g., polysulfone) and stored in a sealed container to prevent carbon dioxide uptake and formation of carbonate. As seen in Figure 7, Pu concentrations of ~10⁻⁴ M are readily attained. The Pu(V) oxidation state and concentration is conveniently monitored by spectrophotometry.

Hexavalent Pu may be prepared by refluxing Pu(IV) near boiling in 1 M HNO₃ for four hours followed by careful complete evaporation of all liquids and re-dissolution in 0.5 M HNO₃. Any remaining Pu(IV) (typically <1%) in Pu(VI) can be determined spectrophotometrically by the major Pu(IV) peak at 476 nm.

The acidic Pu(VI) stock solution must be used within 10 days or be regenerated, as Pu(VI) spontaneously reduces to Pu(IV) with time by radiolysis.

NaOH-bearing Pu(V) test solutions may be prepared by directly adding aliquots of the Pu(V) stock to NaOH solutions, taking care to account for the high NaOH concentrations present in the Pu(V) stock. Preparation of Pu(VI) alkaline test solutions will require additional care, as the Pu(VI) nitrate stock solution is acidic, generating localized heating upon addition to the NaOH solution. Initial precipitation of the sodium plutonate salts also will occur, requiring rapid stirring to bring into solution. For both Pu(V) and Pu(VI) alkaline solutions, carbonate, as Na_2CO_3 , may be added as appropriate using the dry reagent powder.

In all Pu-bearing alkaline test solution preparations, the potential presence of colloidal Pu-bearing solids cannot be excluded. Therefore, removal of these solid phases by ultrafiltration using caustic-resistant filter media is essential. Polysulfone ultrafilter media generally are used, as this polymer shows very high resistance to attack by the NaOH solution and is hydrophilic, readily passing the clarified solution.

6.2 Pu Solubility under Highly Reducing Conditions

The above narrative suggested that the concentration of dissolved Pu in the five column tests may have exceeded that established by the solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ dissolving as Pu(IV) species and that the Pu concentration above $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ observed in prior testing at ≤ 6 M NaOH, even in the presence of hydrazine (see Figure 7), may be orders of magnitude too great. Therefore, some $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ solubility tests with and without added reductants are proposed to establish whether, indeed, Pu is susceptible to chemical reduction and thus create lower-solubility solids.

The tests will be run by spiking known quantities of acidic Pu(IV) nitrate stock into NaOH solutions of various concentrations (suggested range 0.5 to 6 M) with and without various chemical reducing agents. Planning includes the use of reducing agents used in prior testing for U(IV) and Np(IV) hydrated oxide solubility, including zinc metal, iron metal, and sodium dithionite. Tests with hydrazine addition also will be performed. The test items will be kept in tightly capped plastic (polyethylene) bottles with the air excluded, and will be agitated gently to encourage equilibration. At selected contact times (e.g., 1, 3, 7, and 14 days), small aliquots will be withdrawn, the suspensions ultrafiltered, and the sample solutions analyzed for Pu concentrations and compared with the findings shown in Figure 7 and related studies.

It is important not to exclude the possibility of Pu sorption onto the reductant metal solids, particularly those of Fe. Therefore, greater importance and significance will be assigned to findings from the dithionite and hydrazine tests. The results from these tests will help determine whether Pu in ≤ 6 M NaOH solutions follows the solubility limits indicated in Figure 7 and thus behaves as what has been assumed to be Pu(IV) in solution, or follows a lower solubility limit, which may indicate the presence of reducible Pu (e.g., Pu(V)) instead.

6.3 Pu Solubility in the Presence of Silicate

To test Pu solid-phase solubility in the presence of silicate, we will perform tests analogous with those described above for Pu solid-phase solubility in the presence of reducing agents. Test design includes

running a variety of NaOH concentrations (e.g., 0.5 to 6 M) in the presence of 0.05 M sodium silicate, Na₂SiO₃, with orthogonal tests at 2 M NaOH and a range of Na₂SiO₃ concentrations (e.g., 0.02 to 1 M).

Again, the tests will be performed by spiking known quantities of acidic Pu(IV) nitrate into polyethylene vials containing NaOH/Na₂SiO₃ solutions of selected compositions. In either case, the Pu will be added at stoichiometric deficiency with respect to silicate to ensure solubility can be established with the purported ~1:1 Pu:silicate compound. With air excluded, the vials will be tightly capped, agitated, and sample aliquots withdrawn periodically (e.g., 1, 3, 7, and 14 days) for ultrafiltration and analysis of dissolved Pu concentration.

Data from these tests will indicate the degree to which silicate affects Pu solution concentration in NaOH solution. Analyses of the solid phases by coupled scanning electron microscopy (SEM) and EDS, and separately by XRD, also may be performed to characterize the solids.

6.4 Batch Contact Tests

Laboratory experiments are proposed that will examine the uptake of Pu onto glass and onto as-received and treated sRF.

6.4.1 Pu Uptake onto Glass

The preceding sections have noted that each of the five column tests were conducted using glass columns, that glass is attacked and partially dissolved in NaOH solution, and that solid Pu silicates can form in strongly alkaline solution in preference to PuO₂·xH₂O. Therefore, potential sorption or precipitation of Pu onto glass will be examined in this testing.

In these tests, pieces of glass of the same source as the glass used in the PNNL column testing and of known surface area will be exposed to Pu(IV)-spiked NaOH solution at the same NaOH concentrations (e.g., 0.5 to 6 M) as used in the tests with the strong chemical reductants. However, no reductants will be added. The test solutions will be prepared by adding small portions of acidic Pu(IV) nitrate spike to the NaOH solutions at the selected concentrations. After five days of contact, the solutions will be ultrafiltered and each of the treated solutions apportioned to two separate polyethylene vials.

Pieces of glass of known surface area and mass will be added to one of the filtered test solutions at each NaOH concentration. The solutions in the parallel tests with and without glass will be sampled, ultrafiltered, and analyzed periodically (e.g., 1, 3, 7, and 14 days). The Pu concentrations found in the test solution with glass will be compared with those observed in the test solutions without glass. The condition of the glass pieces will be examined at the end of these contacts and SEM/EDS examination of the glass surfaces will be performed to determine Pu distribution on the surface and alteration in the surface texture. Results from these tests should indicate whether surface deposition of Pu onto glass occurs to an extent sufficient to affect the sRF testing outcomes and, more specifically, whether Pu solution concentration is attenuated by the presence of glass.

6.4.2 Pu Uptake onto Fresh Na⁺-Conditioned sRF Resin

Batch contact ion-exchange testing of Pu uptake from solution onto Na⁺-conditioned sRF resin will be undertaken at a variety of NaOH concentrations (e.g., 0.5 to 6 M). The Pu-bearing solutions will be prepared in the same manner as described in Section 6.4.1 above. Thus, the test solutions will be prepared by adding small portions of acidic Pu(IV) nitrate spike to the NaOH solutions at the selected concentrations. After five days of contact, the solutions will be ultrafiltered and each of the treated solutions apportioned to two separate polyethylene vials.

Sodium-conditioned sRF resin will be prepared by treating as-received sRF according to the standard cycling treatment regimen as specified in Nash (2004) and the batch contact testing performed according to the protocols specified by Walker (2004).

Weighed portions of the conditioned and drained resin will be added to one of the prepared vials containing the Pu-bearing NaOH solution of the matching NaOH concentration (e.g., the 0.5-M NaOH-treated sRF will be added to one of the portions of 0.5 M NaOH Pu-bearing spike solution) for each of the selected NaOH concentrations. The other vial for each NaOH concentration will serve as the control. The importance of excluding dissolved and atmospheric oxygen by making up solutions using degassed boiled water and conducting the contacts under inert gas purging and containment in inerted enclosures will be considered in final design of these tests.

The vials with and without added Na⁺-form resin will be agitated and solution samples of each vial taken periodically (e.g., at 1, 3, 7, and 14 days), the sampled solutions ultrafiltered, and the filtrates analyzed for Pu concentration. The solution concentrations will be compared to determine the degree of Pu uptake onto the sRF resin as functions of time and NaOH concentration. Measurements of the system electrode potential will be made to determine whether reducing conditions are established by the resin.

6.4.3 Pu Uptake onto Strong Nitric Acid-Treated and Na⁺-Conditioned sRF Resin

This test series will be performed in the same manner as that outlined in the previous section, but with sRF resin that has first been treated with strong (6 M) HNO₃ as a means to oxidize any readily available reductants present on the resin. The HNO₃ treatment will be conducted in a single batch at room temperature and will last for two hours with agitation occurring every 10 minutes. After the strong HNO₃ contact, the excess acid will be drained, the resin water-washed twice to remove residual interstitial HNO₃, and then the resin will undergo the same conditioning regimen outlined above for the sRF.

The Pu-bearing solution contacts then will be conducted using precisely the same experimental procedure as outlined in the previous section.

The Pu uptake test results for the strong HNO₃-treated and Na⁺-conditioned sRF resin, in comparison with the results found in the parallel tests without the resin treatment with strong HNO₃, will indicate whether residual reductants on the resin are responsible for the observed Pu uptake. Again, measurements of electrode potentials will be made to determine whether reducing conditions are established by the resin.

The reductive capacity of the sRF medium before and after the treatment with strong HNO₃ also can be evaluated by measuring consumption of known amounts of tetravalent cerium, cerium(IV) (Um et al.

2015). However, alternative methods (including less aggressive oxidants) may be necessary, as the resin itself is susceptible to destruction by strong oxidants.

6.5 Characterization of Pu Uptake onto sRF Resin

The nature of the interaction of Pu with the sRF resin lies at the heart of the issue of Pu uptake and retention onto sRF. Therefore, characterization of the Pu-loaded sRF resin is indispensable to answering the following questions:

- Is the Pu retained due to the chemical interaction with the RF medium or is the Pu physically trapped due to the sRF beads shrinking upon conversion to the H^+ form? This may be scoped by determining how the sRF bead morphology and surface area change upon conversion to the H^+ form.
- Is the Pu uniformly distributed within the sRF bead (indicating ion exchange uptake) or does it form localized heterogeneous deposits (indicating a solid-phase filtration mechanism)?
- What is the dominant oxidation state of Pu retained by the resin?

This investigation will use two different techniques to examine physical cross-sections of the Pu-loaded sRF beads exposed to the Pu-bearing NaOH solution before and after stripping with HNO_3 , and thus corresponding to the resin Na^+ and H^+ forms. The Pu-loaded resins will be obtained from the batch contact tests described in the two previous experimental sections of this report.

The physical distribution of the Pu within the resin will be determined by SEM imaging and EDS elemental mapping. The resin beads likely will need to be mounted in epoxy and the epoxy casting sectioned and polished according to standard mineral and metal imaging techniques. The SEM images will provide information on the evolution of bead morphology upon conversion to the H^+ form. Elemental mapping by EDS will be used to qualitatively determine the distribution of Pu in the bead before and after stripping to answer questions regarding the presence of Pu in the diffuse or localized particulate form and will provide quantitative elemental analysis of the selected areas of interest.

If Pu particulates are identified on the resin, the ionizing-radiation Quantum Imaging Detector (iQID) recently developed at PNNL (Miller et al. 2014) will use single-particle digital autoradiography to analyze the cross-section of a Pu-loaded sRF resin bead to determine the spatial distribution of Pu particulates within the bead. This technique provides information on the localized particles emitting ionizing radiation and enables quantification of radionuclides at low activity levels (0.1 Bq; 0.1 disintegration/second), as well as characterization of the Pu spatial profile at resolution on the order of tens of microns. Further high-resolution information on the presence of Pu particles can then be obtained by sampling Pu-rich areas of interest identified by iQID using focused ion beam SEM coupled with transmission electron microscopy

X-ray photoelectron spectroscopy (XPS) can be used to determine the oxidation state of Pu in the sRF environment. A recent review article indicates that XPS is a powerful technique to study actinides, and Pu in particular, and provides a wealth of information on the physicochemical states of the actinides including oxidation states, electronic configurations, and the nature of chemical bonding in compounds and within solid materials (Teterin and Teterin 2004).

If sufficient Pu concentration in the sRF resin is sufficiently high, the Pu oxidation state and chemical environment also can be characterized by optical reflectance spectroscopy.

The specific surface area and pore volume of the sRF beads in the Na⁺ and H⁺ forms can be determined by the BET (Brunauer-Emmitt-Teller) nitrogen adsorption method, but this may be challenging due to bead shrinkage on drying for the BET test. This analysis will provide information on change of the physical properties of the resin upon its conversion to the H⁺ form leading to the potential physical trapping of Pu in the polystyrene coating of the bead.

6.6 Enhanced Pu Stripping from the sRF

Many of the effects of Pu uptake onto the sRF resin can be obviated by more thorough stripping of the adsorbed or included Pu from the resin. Various means to achieve enhanced Pu stripping are described in this section, bearing in mind the potential alternative mechanisms of Pu association. Finally, a program to test these various enhanced Pu stripping methods is outlined.

6.6.1 Potential Pu Stripping Agents

The efficiency of Pu stripping from the loaded sRF resin can likely be improved by adding a complexant to the 0.5 M HNO₃ eluting agent. The validity of such an approach has been demonstrated previously in that the uptake of Pu(IV) by the Dowex 50W×8 cation ion-exchange resin (gel styrene-divinylbenzene sulfonate resin) has been quantitatively decreased by use of a pH 4 citrate buffer. This decrease was attributed to the formation of 1:1 Pu-citrate complex (Table 6; Kantar and Honeyman (2005)). However, complexation of Pu by citrate at low pH is expected to be suppressed due to the weakly acidic nature of the citric acid leading to its being protonated.

Table 6. Complex Formation Constants for Pu(III, IV) with Various Ligands

Ion	Complexant	Complex Stability Constants				Conditions	Ref*
		logβ ₁	logβ ₂	logβ ₃	logβ ₄		
Pu(IV)	Citric acid	16.53				0.1 M NaCl, pH 4, 22°C	1
		6					
		14.71	19.92			Zero ionic strength, 25°C	2
Pu(IV)	TMDGA	0.84	2.06	4.81		1 M NaNO ₃ , 1 M HNO ₃ , 25°C	3
		2.16	3.53	4.53		0.6 M NaNO ₃ , 3 M HNO ₃ , 25°C	
Pu(IV)	DMOGA	6.52	9.14	15.77		0.5 – 0.8 M HClO ₄ , 25°C	4
Pu(IV)	AHA	14.2				1.52 M NaClO ₄ , 0.48 M HNO ₃	5
			24.1	32.2		2 M NaClO ₄	
Pu(III)		5.77	11.66	14.83	15.84		
Pu(IV)	HF	8.43				Extrapolation to infinite dilution of the averaged values obtained in 1 M HClO ₄	6
Pu(III)		4.19					
Pu(IV)		7.61	14.77	20.11	26.07	1 M NaClO ₄ , 19°C	7
		8.86	15.91			Extrapolation to infinite dilution of the values obtained in 2.2 M HClO ₄ , 25°C	8

* 1: Kantar and Honeyman (2005); 2: Raymond et al. (1987); 3: Wei et al. (2012); 4: Hang et al. (2005); 5: Carrott et al. (2007); 6: Table 8 of Chaudhuri et al. (1999); 7: Sawant et al. (1990); 8: Xia et al. (2010)

This brief overview provides information on potential Pu-complexing eluting agents to amend the 0.5 M HNO₃ solution currently used to strip and regenerate the sRF resin. The candidate eluting agents are shown in Figure 17.

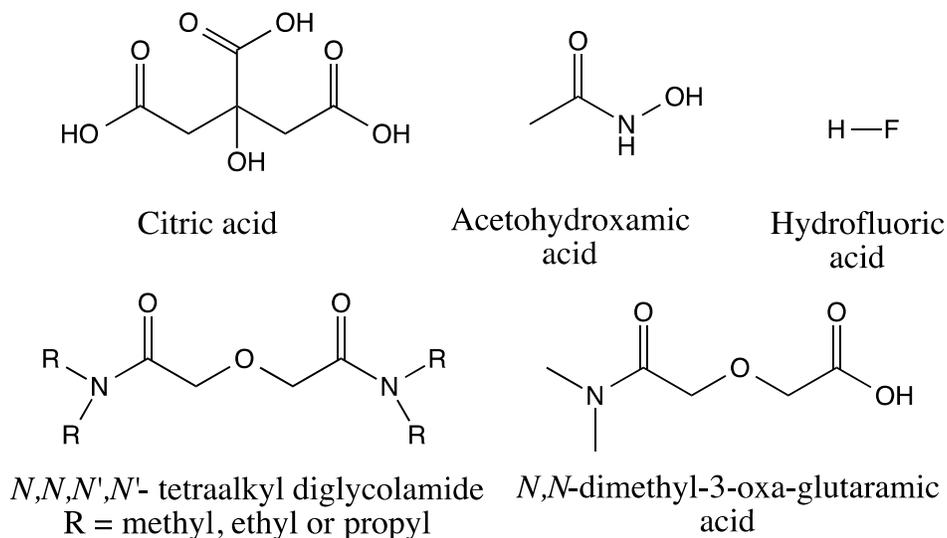


Figure 17. Chemical Structures of Proposed Eluting Agents for Pu from sRF

Complexation of Pu in acidic solutions can be achieved using water-soluble, neutral or strongly acidic ligands. One such class of neutral water-soluble ligands is tetraalkylated diglycolamides (DGA) including methyl, ethyl and propyl derivatives. Wei et al. (2012) recently investigate the complexing properties of the neutral *N,N,N',N'*-tetramethyl diglycolamide (TMDGA) ligand with tri- and tetravalent actinide ions. They reported complex formation constants, shown in Table 6, that indicate solution acidity affects performance of TMDGA only slightly. The authors note, however, that TMDGA forms rather weak complexes with Pu, presumably due to the competitive processes of hydration and nitrate coordination. Despite this finding, a systematic investigation of various water-soluble chelators for stripping actinide ions using HNO₃ solutions from the loaded *N,N,N',N'*-tetraoctyl diglycolamide *n*-dodecane organic phase concluded that DGA ligands are significantly stronger complexing agents, for actinide ions in general and Pu(IV) in particular, than multidentate carboxylic and aminopolycarboxylic acids (Sasaki et al. 2007). Addition of as little as 10 mM of DGA in aqueous 0.25 M HNO₃ solution quantitatively recovers Pu(IV) from the organic solution and prevents its re-extraction. The authors recommend *N,N,N',N'*-tetraethyl diglycolamide (TEDGA) for the practical applications based on its solubility in water, high recovery for reuse using primary alcohol extraction (may not be practicable in the LAWPS), and its commercial availability.

Replacement of one amide group of DGA with carboxylate produces the acidic monoamide *N,N*-dimethyl-3-oxa-glutaramic acid (DMOGA) ligand. This ligand strongly complexes Pu(IV) in acidic solutions (Table 6; Hang et al. (2005)). The enhanced stability constants for Pu(IV)·DMOGA complexes compared to the TMDGA analogs can be attributed to both the contribution of ionic bonding to the covalent coordination and to the favorable entropic effect due to release of the carboxylate hydration water upon binding of the actinide ion (Tian et al. 2009). It is noted, however, that DMOGA's complexing ability is affected by the solution acidity, and somewhat suppressed when HNO₃ concentration approaches 1 M, as demonstrated in solvent extraction studies (Zhang et al. 2007).

Hydrophilic hydroxamic acids also are promising eluting agents, as they not only simultaneously complex Pu in various oxidation states but also reduce Pu(IV) to Pu(III). Application of formo- and acetohydroxamic acids (FHA and AHA, respectively) in separation processes relevant to the reprocessing of used nuclear fuel has been extensively investigated (Nuñez and Vandegrift 2001). In particular, AHA has been considered as an aqueous hold-back reagent to prevent extraction of Pu and neptunium by tri-*n*-butyl phosphate in the UREX process, allowing selective separation of U and Tc from dissolved used nuclear fuel.

Carrott et al. (2007) investigated the affinity of acetohydroxamic acid for Pu(IV) and Pu(III) ions and determined corresponding complex stability constants (Table 6). They observed that in moderately acidic solution with $[H^+] \approx 0.5$ M, a stable mono-acetohydroxamic $[Pu(IV) \cdot AHA]^{3+}$ complex dominates, and formation of the higher order complex species takes place as solution acidity decreases. The complexation of Pu(IV) by AHA is accompanied by Pu(IV) reduction to Pu(III). The Pu(III), in turn, forms 1:1, 1:2, 1:3, and 1:4 complexes with AHA.

The reduction potential of the Pu(IV)/Pu(III) couple in the presence of AHA in nitric acid solutions has been studied in detail, and several reaction mechanisms proposed (Tkac et al. 2009). Introduction of AHA into HNO₃ solution initiates formation of the $[Pu(IV) \cdot AHA]^{3+}$ complex, which decomposes and forms Pu(III) via a second-order process with respect to the $[Pu(IV) \cdot AHA]^{3+}$ concentration. AHA can also reduce uncomplexed Pu(IV) to Pu(III). In turn, Pu(III) is unstable and easily oxidizes back to Pu(IV).

One drawback of using AHA as an eluting agent for sRF resin is that under acidic conditions it undergoes fast and irreversible hydrolysis and decomposes to generate carboxylic acid and hydroxylamine products (Chung and Lee 2006). The AHA hydrolysis was found to follow first-order dependence on hydronium ion concentration so that in 1 M HNO₃, about 50% of the AHA decomposes in 7.5 hours at 25 °C. The rate of decomposition significantly increases at elevated temperatures.

Hydrofluoric acid (HF) strongly complexes with Pu in various oxidation states and is often used in combination with HNO₃ to facilitate Pu oxide dissolution (Barney 1977; Tallent 1976). The complexation behaviors of Pu(IV) and Pu(III) with fluoride have been extensively investigated and several studies report association constants obtained under different conditions and different experimental methods (Chaudhuri et al. 1999). Only formation of the 1:1 PuF^{3+} complex has been examined in the majority of the studies and reported values demonstrate good agreement across the tested methods. Table 6 lists the average formation constant value obtained for 1 M HClO₄ and extrapolated to infinite dilution. Comparison of the reported association constants indicates that the formation of the PuF^{3+} complex depends little on solution acidity, as nearly identical values are observed for neutral and acidic solutions up to 2 M HClO₄ or HNO₃ (the highest acidity of the tested solutions). Recent study of Pu(IV) complexation with fluoride reported consistent results (Xia et al. 2010). Few studies report formation of the 1:2 complex species and only one study reports formation of higher order species (Table 6).

The reviewed literature information suggests that several water-soluble complexing agents with high affinity for Pu(IV) exist in acidic solution. Each of these might be used as Pu eluting agents to amend the HNO₃ stripping solution utilized for Cs⁺ elution from sRF resin. The selection of eluting agent will depend on several factors, including the mechanism of Pu retention on the sRF resin, availability, cost, and downstream processing constraints. If the interaction of Pu(IV) with alcohol functional groups (resorcinol, catechol, phenol) and formation of the coordination complexes is responsible for Pu retention,

application of the complexing neutral TEDGA could be sufficient. If Pu retention by the resin is by reduction and/or formation of insoluble precipitates, HF or AHA could be more efficient.

6.6.2 Testing of Potential Pu Stripping Agents for sRF Resin

The performance of chelation and complexation stripping using three candidate eluting agents will be evaluated in the batch contact experiments using Pu-loaded sRF resin (see Section 6.4.2). The three agents to be tested include commercially-available TEDGA, AHA, and HF. In these experiments, sRF resin containing Pu loaded from alkaline solutions as described in Section 6.4.3, and containing known amounts of Pu (nanocuries of Pu per gram of resin) will be contacted with the 0.5 M HNO₃ stripping solution with or without the selected eluting agent.

The following tests are envisioned to evaluate efficiency of Pu removal from the sRF resin.

Test 1 – Selection of the best performing eluting agent. In this experiment, Pu-loaded sRF resin will be equilibrated with 0.5 M HNO₃ solution containing no (control sample) or variable (0.005 to 0.1 M) TEDGA, AHA, or HF at room temperature for 24 hours. The amounts of Pu eluted into the solution phase will be quantified by liquid scintillation counting. The best performing candidate eluting agent identified will be used for follow-up testing in Tests 2 and 3.

Test 2 – Acid sensitivity test. The performance of the selected eluting agent as a function of HNO₃ concentration in the stripping solution will be tested. The Pu-loaded sRF resin will be equilibrated with 0.1 or 1 M HNO₃ solution containing no (control sample) or fixed concentration of the eluting agent determined in Test 1 at room temperature for 24 hours. The results from this test will be compared with the Pu stripping efficiency using 0.5 M HNO₃ solution containing the same concentration of eluting agent.

Test 3 – Effect of the chelation stripping on Cs removal by sRF resin in the cycle tests. Samples of the sRF resin equilibrated with HNO₃ solution with or without selected eluting agent will be converted to the sodium form and tested for Cs removal from simulated tank-waste solution. The resulting Cs K_d values will be compared.

Any promising eluent would need a fourth test to establish the reliability of the Pu removal through multiple column loading and elution cycles.

7.0 Conclusions

Scientists at both PNNL and SRNL have observed the uptake and retention of Pu onto sRF resin columns during ion-exchange testing of Cs removal from actual alkaline tank waste. This behavior has raised criticality safety concern in the Cs removal unit operation of the LAWPS pretreatment steps. As a first step to address these issues, the present report has summarized studies of the technical reports related to the Pu uptake and retention and broader studies of scientific literature regarding other instances of Pu uptake from alkaline tank-waste solution, as well as review of Pu chemical behavior in alkaline media and consideration of potential means whereby Pu might be retained on the sRF resin.

Five separate Cs removal laboratory tests of filtered alkaline tank waste from the Hanford and Savannah River Sites have shown incorporation and retention of Pu onto sRF and RF. The retention of dissolved Pu from these actual wastes onto the four sRF and one RF resin columns in the five test series ranged from about 2 to 38% of the input quantities; the amount of Pu remaining on the resin after elution using 0.5 M HNO₃ ranged from 0.2 to 9.4% of the input. Uranium also was retained in some tests (near 0 to ~9% of the input quantities). For both Pu and U, the retention on the cation-exchanging RF resins was unexpected because both metals are expected to be present in the alkaline tank-waste solution as various types of anionic hydroxide-complexed species.

Substantial retention of Pu onto other organic ion-exchange media that have been used to remove Cs from alkaline radioactive tank waste also has been observed for SuperLig-644 (a crown ether-type functional group) in tests performed at PNNL and for ARC-359 (a sulfonated phenol-formaldehyde cation exchange resin) in tests performed at the Savannah River Laboratory. Although ARC-359 was used in full-scale plant operations to remove Cs from millions of liters of Hanford Site tank waste, no information on Pu retention in these process operations was found in the technical literature or historic operating records. Screening studies of ion-exchange resins and various solids sorbents were conducted at LANL using simulated Hanford-type wastes, including one test series that contained Pu in simulated complexed concentrate alkaline waste. However, the LANL studies reported little Pu uptake onto phenol-formaldehyde resin (CS-100), an RF resin (BSC-210), or Superlig-644.

The bases for criticality concern arising from the Pu retention also were examined in this report. At maximum acceptable dissolved Pu concentrations ($\sim 2 \times 10^{-6}$ M), and fractions of Pu found to be retained on the sRF resin in laboratory testing, Pu loadings onto the ion exchange columns can approach the 360-grams-of-Pu criticality safe mass limit, but this occurs only under extremely extended process operation throughputs. The retention of a sizable fraction of the loaded Pu after normal elution operations similarly leads to concern in exceeding the 360-gram limit. Criticality engineers have also broached the possibility that Pu loading onto the sRF columns was due to Pu-bearing particle filtration.

The chemical behavior of Pu in alkaline media is complicated by

- the availability of three accessible oxidation states in solution,
- the sensitivity of Pu concentration in solution to the redox condition of the solution,
- the stability of the Pu(IV) hydrated oxide solid phase, and also the potential availability of less-soluble Pu silicate solid phases, and

- the coprecipitation and sorption of Pu within and onto sludge solid phases, including those of robust and available neutron absorber elements including Fe and U.

This report briefly reviewed the chemistry of Pu in alkaline media to set the stage for further discussions and considerations of laboratory experimentation. Herein are also described the Pu concentrations actually observed in the solution, sludge, and salt cake fractions of Hanford tank waste and the marked propensity for Pu to distribute to the sludge solids. The broad range of Pu solution concentration and sensitivity to solubilization by carbonate complexation also are noted.

Based on the sRF and other ion-exchange resin test observations, the properties of the RF and sRF resins, and the known chemistry of Pu in alkaline media, this report proposed the following several potential mechanisms for the Pu uptake and retention:

- Solid-solution separation arising because of Pu being present in finely divided solids.
- Formation of less-soluble Pu solids from more soluble higher oxidation state Pu upon contact with chemical reductants within the sRF resin.
- Chemical reduction of dissolved Pu by radiolysis reactions to form lower oxidation state and less soluble Pu.
- Precipitation of Pu as a silicate with silica arising from attack of the glass ion exchange columns by alkaline solution.
- Pu sorption or ion exchange onto catechol impurities (which may act as bidentate chelating agents) in the sRF resin.
- Pu entrapment by resin channel collapse during shrinkage occasioned in resin elution by acid (deemed unlikely).

In the absence of a known reason for the observed Pu uptake and retention, a program of laboratory experimentation is proposed to help identify the operant mechanism(s) and thus guide a technically defensible path forward to resolve the underlying criticality safety issue. The proposed laboratory test program is arranged to conduct simpler and less costly batch tests initially and then use the results from these early tests to inform the necessity and guide the extent of any further experimentation, such as column testing.

The variety of potential means by which Pu may become associated with, and retained on, the sRF and sRF columns dictates a broad variety of simple tests for these initial laboratory efforts. These proposed relatively simple experiments are designed to investigate the above potential mechanisms for Pu uptake and retention as well as to measure Pu solubility under strongly reducing conditions and in the presence of silicate. Batch contact tests with glass and with sRF resin under controlled conditions are proposed and would be supplemented with characterization of resin loaded with Pu. Finally, we propose testing of an alternative means to elute Pu from the sRF columns and thus eliminate Pu retention.

8.0 References

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Appendix A

Presentation

“Criticality Safety for the Pu Retained in IX”

**by David Losey, Criticality Safety Engineer,
Washington River Protection System WRPS**

4/19/2016



Criticality Safety for the Plutonium Retained in IX

Supporting development of a preliminary
Criticality Safety Evaluation Report (CSER) for LAWPS

David Losey
WRPS Criticality Safety Engineer
4/19/2016

Plutonium Inventory Inputs

- ▶ **0.5 mg/L** limit on ^{239}Pu concentration for output feed to WTP (ICD-30)
- ▶ sRF resin testing at Savannah River (SRNL-STI-2009-00605)
 - ▶ **38%** Pu retention in initial cycle loading
 - ▶ **10%** Pu retention post-elution for single cycle
- ▶ **360 g** criticality safe mass limit ^{239}Pu (24590-WTP-Z0C-W11T-00014)
 - ▶ Conservative -- based on optimal moderation, geometry
 - ▶ Preliminary -- can be increased for factor of 3 - 4 with computations

IX Plutonium Retention

- For example, 20 days operation at 17 gpm

$$0.5 \text{ mg/L Pu} \times 38\% \times 20 \text{ days} \times 17 \text{ gpm} \times \text{conversions} = \mathbf{352 \text{ g}}$$

c.f. 360 g safe limit

- Retained on column post-elution, single cycle

$$10\% / 38\% \times 352 \text{ g} = \mathbf{92 \text{ g}}$$

- Does 10% retention hold for subsequent multiple cycles?

$$4 \text{ cycles} \times 92 \text{ g} = \mathbf{368 \text{ g}}$$

sRF Resin Performance

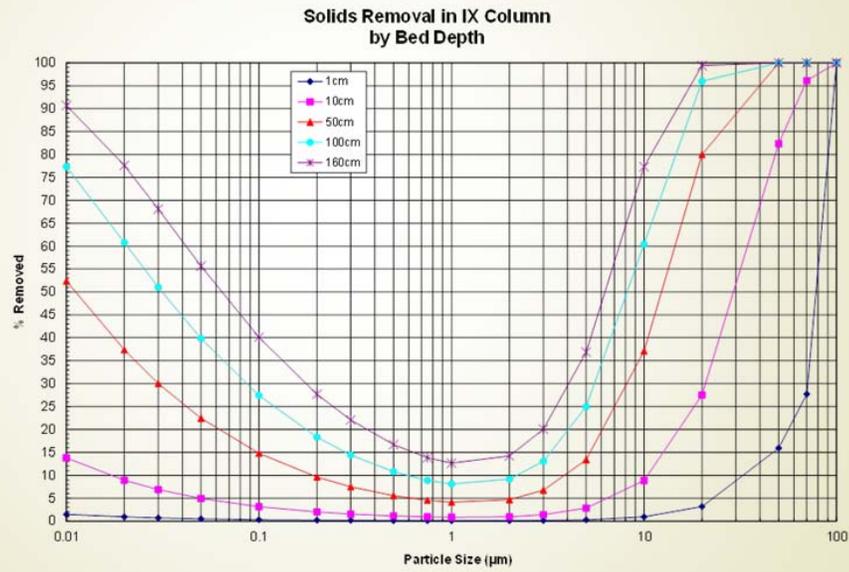
4

	Initial Pu Retention	<i>elu</i> ate	Post Elution Pu Retention (single cycle)	Year	Notes
SRNL-STI-2009-00605	32 - 43%		10%	2009	Dissolved saltcake, with ²³⁸ Pu
PNNL-18007	4.5%		0.2%	2009	REDOX sludge, saltcake
WTP-RPT-134		9%		2006	AP-101 waste
WTP-RPT-135	12%	1.7%		2006	AN-102 waste

sRF Resin Performance

- ▶ Testing shows highly variable and significant Pu retention
- ▶ Essentially no data on multi-cycle Pu retention
 - ▶ May be limiting condition
- ▶ **PNNL-23717** - “dissolved Pu species in alkaline waste are anionic (negatively charged) and highly unlikely to be attracted to the IX media, which are designed to attract the positively charged cesium ion, Cs⁺.”
- ▶ Pu retention mechanism could be other than IX, e.g. filtration, surface, electro-static?
 - ▶ SRNL IX test filtered to 0.2 μm,
 - ▶ LAWPS tube pores 0.1 μm
 - ▶ *Pu/Fe size 0.02 μm, RPP-RPT-58509*

1 μm Particles Transit Columns



sRF resin test references

- ▶ SRNL-STI-2009-00605, *Characterization of Cycled Spherical Resorcinol-Formaldehyde Ion Exchange Resin.*
- ▶ PNNL-18007, WTP-RPT-171, Rev. 0, *Laboratory Demonstration of the Pretreatment Process with Caustic and Oxidative Leaching Using Actual Hanford Tank Waste.* Pacific Northwest National Laboratory, Richland, WA.
- ▶ PNNL-23717, Rev. 1 WTP-RPT-235, Rev. 1 *Effects Influencing Plutonium-Absorber Interactions and Distributions in Routine and Upset Waste Treatment Plant Operations.*
- ▶ WTP-RPT-134, Rev 0, *Spherical Resorcinol-Formaldehyde Resin Testing for ¹³⁷Cs Removal from Simulated and Actual Hanford Waste Tank 241-AP-101 Diluted Feed (Envelope A) using Small Column Ion Exchange (24590-101-TSA-W000-0004-174-00001, Rev 00A).*
- ▶ WTP-RPT-135, Rev 1, *Small Column Ion Exchange Testing of Spherical Resorcinol-Formaldehyde Resin for ¹³⁷Cs Removal from Pre-Treated Hanford Tank 241-AN-102 Waste (Envelope C) (24590-101-TSA-W000-0004-72-00017, Rev 00B).*
- ▶ WTP-RPT-144, Rev 0, *Spherical Resorcinol-Formaldehyde Resin Analysis following Actual Hanford Tank Waste Processing (24590-101-TSA-W000-0004-114-00020, Rev 00A).*
- ▶ RPP-RPT-58509, Rev. 0, *Solids Properties in Tank Waste for the Low Activity Waste Pretreatment System Feed.*

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