Sorption of Uranium, Plutonium and Neptunium onto Solids Present in High Caustic Nuclear Waste Storage Tanks

Authors:

Lawrence N. Oji
Savannah River National Laboratory
Washington Savannah River Company
Aiken, SC 29808
Phone: (803)-725-5328
Fax: 803-725-1660
E-mail: lawrence.oji@srnl.doe.gov

Lawrence N. Oji (BS, Mathematics, Trinity College, Deerfield ILL, 1980; Ph.D. Physical chemistry, The University of Arkansas, Fayetteville, 1986) is a Principal Research Scientist at the Savannah River National Laboratory (SRNL). He has more than 12 years of industrial research experience in ion-exchange characterization and application, chemistry of high-level waste and stabilization of radioactive waste. Current research interests include chemistry of cesium, tritium, actinide and mercury "getters" and chemistry of aluminosilicates in nuclear waste processing.

William, R. Wilmarth
Savannah River National Laboratory
Washington Savannah River Company
Aiken, SC 29808

William R. Wilmarth (BS, Chemistry, Clemson University, Clemson, SC, 1983; Ph.D. Inorganic and Radiochemistry, University of Tennessee, Knoxville, TN, 1988) is a Group Leader in the Chemical Science and Technology section of the Savannah River National Laboratory. He has more than 20 years of nuclear-related industrial and academic experience. Current research interests include the chemistry of the actinides in highly alkaline radioactive wastes, advanced characterization techniques to examine exotic radionuclides in a variety of solid and liquid matrices, and chemical processing of High Level Wastes to afford final disposition options.

David T. Hobbs
Savannah River National Laboratory
Washington Savannah River Company
Aiken, SC 29808

David T. Hobbs (BS, Chemistry, University of North Carolina at Chapel Hill, 1974; Ph.D. Inorganic chemistry, Vanderbilt University, 1979) is an Advisory Scientist at the Savannah River National Laboratory (SRNL) with more than 20 years of experience in the characterization and chemistry of high-level nuclear waste. Current research interests include a better understanding of actinide and inorganic chemistry associated with high-level nuclear waste, development of improved pretreatment processes and in situ characterization techniques.

Total number of pages: 26

Total number of Figures: 11

Total number of Tables: 3

ABSTRACT

Solids such as granular activated carbon, hematite and sodium phosphates, if present as sludge components in nuclear waste storage tanks, have been found to be capable of precipitating/sorbing actinides like plutonium, neptunium and uranium from nuclear waste storage tank supernatant liqueur. Thus, the potential may exists for the accumulation of fissile materials in such nuclear waste storage tanks during lengthy nuclear waste storage and processing.

To evaluate the nuclear criticality safety in a typical nuclear waste storage tank, a study was initiated to measure the affinity of granular activated carbon, hematite and anhydrous sodium phosphate to sorb plutonium, neptunium and uranium from alkaline salt solutions. Tests with simulated and actual nuclear waste solutions established the affinity of the solids for plutonium, neptunium and uranium upon contact of the solutions with each of the solids. The removal of plutonium and neptunium from the synthetic salt solution by nuclear waste storage tank solids may be due largely to the presence of the granular activated carbon and transition metal oxides in these storage tank solids or sludge. Granular activated carbon and hematite also showed measurable affinity for both plutonium and neptunium. Sodium phosphate, used here as a reference sorbent for uranium, as expected, exhibited high affinity for uranium and neptunium, but did not show any measurable affinity for plutonium.

I. INTRODUCTION

Over 90 million gallons of High-level radioactive and caustic chemical liquid and sludge wastes are currently stored at the Savannah River and Hanford sites, which are U.S. Department of Energy (DOE) facilities. These radioactive wastes are stored in large underground carbon steel tanks and were accumulated over 60 years of chemical processing for the production of nuclear materials including plutonium, tritium and enriched uranium.

In general, the irradiated target and fuel assemblies were first dissolved in nitric acid. After dissolution several different separation processes such as precipitation, ion exchange and solvent extraction were employed to separate and purify the plutonium, neptunium and uranium. After separation of the actinides, the residual materials were discarded to the high-level waste storage tanks. Prior to transfer to the storage tanks, high level waste (HLW) at the Hanford and Savannah River Sites was made strongly alkaline with the addition of sodium hydroxide solution to prevent corrosive attack of the carbon steel tanks.

The addition of the sodium hydroxide results in the precipitation of the bulk of the metallic elements as metal hydroxide and hydrous metal oxides. The precipitated solids, referred to as sludge solids, gravity settled to form a concentrated solids layer in the bottom of the waste tanks. From time to time, other solids were also introduced directly into the storage tanks. These solids included organic and inorganic ion exchange materials, glass frit and carbon black. Other solids such as sodium aluminosilicate minerals are produced as a result of chemical reactions due to the presence of aluminates and silicates in the highly alkaline supernatant media.

Current cleanup efforts are aimed at concentrating the radioactive components of the HLW into a small volume and encapsulating this fraction in a highly durable borosilicate glass wasteform that will be disposed in the federal repository. The remaining decontaminated liquids are incorporated into a low level waste form for onsite disposal. The Tank 50H at the Savannah River Site serves as the receipt tank for low activity waste from pretreatment processing of high-

level nuclear wastes and the Effluent Treatment Facility at the Savannah River Site. Wastes are introduced this tank and stored for a period of time before transferring to the Saltstone facility for disposal.

Recently, visual inspection of this tank revealed the presence of a large quantity of solids. Analysis of these solids identified several components including sodium aluminosilicate, hematite (Fe_2O_3) carbon black, sodium phosphate, etc[1,2]. Some of these solids are known to sorb actinides[3, 4, 5] Thus, there exists the opportunity to accumulate fissile materials in a small volume. The goal of this study was to ascertain whether nuclear waste storage tank sludge materials can precipitate and absorb dissolved actinides like plutonium from nuclear waste storage tank supernatant liquid fraction. Such precipitations of dissolved actinides, if possible and unguarded, could pose criticality concerns during the processing and stabilization of high activity nuclear waste in storage tanks. Thus, to evaluate the nuclear criticality safety associated with the transfer of waste solutions into nuclear waste storage tanks an experimental program was initiated to determine the loading capacities of common fissile elements (plutonium, neptunium and uranium) onto the more prevalent solids present in Tank 50H.

II. EXPERIMENTAL

In these sorption tests, both pure chemicals and solids obtained from a typical nuclear waste tank from the SRS high level waste facility (Tank 50H solids) were used. Hematite (Fisher Scientific) and granular activated carbon, (Duratec International Grade C-200) were used as received without further purification. The anhydrous sodium orthophosphate used in this study was derived from hydrated sodium orthophosphate, $Na_3PO_4.12H_2O$, (Fisher Scientific) by heating of the hydrated salt in stainless steel beaker to above its melting (1340 °C) point for several hours under inert conditions containing argon gas. After cooling, the resulting solid was then transferred to an oven and maintained at 120 °C for one hour before bringing it to room temperature in a desiccator. A pasty Tank 50H core solid sample used in this study was obtained

from Tank 50H. The sample was air dried in a hood for more than 200 hours until a fairly constant weight solid material was obtained. The resulting air-dried Tank 50H solid sample was ground into a powder before use.

Both simulated waste solution and actual tank supernatant solution were used in these sorption tests. The tank supernatant nuclear waste solution was obtained from SRS tanks 37H and 44F. Table 1 provides the composition of the simulated waste solution. Table 2 provides the composition of the composited supernatant samples. Prior to use in these tests, the tank supernatant material had been contacted with monosodium titanate to remove ^{90}Sr and alpha-emitting radionuclides followed by a demonstration of the caustic side solvent extraction (CSSX) process to remove ^{134,137}Cs. After the CSSX demonstration researchers added appropriate quantities of plutonium as Pu(IV), neptunium as Np(V) and uranium as U(VI) to bring the concentration of these components to the values reported in Table 2. Removal of the radio-cesium isotopes reduced the high gamma activity allowing researchers to perform subsequent tests in radiological hoods.

Preliminary sorption tests were performed to verify if tank 50H sludge material and its contents were capable of absorbing actinides. These tests were carried out before the test to determine the sorption isotherms with the tank 50H materials as well as with the pure solids (activated carbon, iron oxide and sodium phosphate). In these initial screening sorption tests involving tank 50H solids in contact with simulated waste solutions three different liquid-to-solid ratios, 3, 5 and 10 (v/w), were used. This range of ratios was used to enhance filtration processing to separate the liquid from the solid fraction after contact and to minimize initial analytical costs. For each of these initial screening tests a constant solids weight of 5.01 ± 0.02 grams was maintained and the volume of the simulant waste varied. All other actinide sorption tests with both tank 50H solids and pure solids in contact with the simulants or real tank waste featured liquid-to-solid ratios ranging from 14:1 to 60:1 (v/w). Loading tests for the pure solids

and the air-dried tank 50H solids involved contacting 0.5 grams of solids with varying quantities of the simulated waste solution (Table 1) in 150-mL capped polypropylene bottles. After combining the solution and solid phases, the test bottle were placed in an orbital shaker (Lab-Line Model C-760) and mixed at 175 rpm for 24 hours at 26 ± 2 ℃. To determine the solution phase actinide concentrations (actinide concentration-final) after 24 hours of contact, samples of the liquid phase were separated from the solid phase using a 0.45-micron nylon filter. A measured aliquot of the filtrate was diluted with 5.0 M nitric acid and analyzed for plutonium, neptunium and uranium by inductively coupled plasma mass spectrometry (ICP-MS). Tests with no added solids or controls (simulant solutions only) were featured in each test set as controls for preparation errors, instrumental biases and unexpected removal mechanisms such as sorption onto polypropylene bottle walls. The controls were also subjected to the same separation and acid dilution techniques described above.

In these sorption test the actinide concentrations per gram of solid sorbent was plotted against the final actinide concentration in solution. To estimate what the maximum actinide loading values are at the plateau region of the curves a second degree polynomial fitting was used for all the loading data (Figures 3 through 10). By equating the first derivatives of each loading capacity equation to zero and solving for x values, the maximum loading capacities (y-values) for plutonium and neptunium were determined. The use of a second degree polynomial fitting function for the loading curve data applies only up to the inflection point of the curve and not beyond that point and only if that point falls within the data set. As a caution, these equations may not be used to extrapolate to values outside the data set.

III. RESULTS AND DISCUSSION

Figures 1 and 2 show plots of the solution phase actinide concentrations at each of the liquid-to-solid ratios for the tank waste and the synthetic waste solutions, respectively, in contact with the Tank 50H solids. A very good agreement between duplicate tests conducted at the liquid to solids ratio of 5:1 was observed. In both graphs, as the liquid-to-solid ratios decreased (i.e., increased Tank 50H solids fraction) the amount of plutonium and neptunium removed from the liquid phase increased as evidence by the lower solution phase concentrations of plutonium and neptunium. Note that uranium concentrations did not change in any of the tests. Thus it was concluded that the Tank 50H solids exhibit an affinity for both plutonium and neptunium, but not for uranium.

After establishing the affinity of the tank 50H solids for plutonium and neptunium a series of tests were performed to determine the loading of plutonium and neptunium onto the tank 50H solids. Figures 3 and 4 provide plots of the amount of plutonium and neptunium, respectively, loaded onto the Tank 50H solids versus the final sorbate concentration in solution. The shape of the loading curve is typical for a Type 1 sorbent. From the loading curves maximum loading capacities of 2.01μg/g for Pu and 4.48 μg/g for Np was derived.

The next set of tests determined the affinity of pure solid components for plutonium, neptunium and uranium in the alkaline salt solutions or simulant. The objective of this series of tests was to determine which components of the tank 50H solids was responsible for the removal of plutonium, neptunium and uranium. These tests used the same experimental protocol as described before with the tank 50H solids except that the simulated waste solution was contacted with the pure solid component, hematite, granular activated carbon or sodium orthophosphate. With the exception of sodium phosphate the solids did not absorb or precipitate measurable amounts of uranium from solution.

Figures 5-8 show the isotherms obtained for the sorption of plutonium and neptunium onto the granular activated carbon and hematite. Figures 9 and 10 show the isotherms for the sorption of neptunium and uranium, respectively, onto sodium orthophosphate. Some of the loading curves presented in the graphs, for example in Figure 8 for loading of neptunium onto hematite, do not have sufficient data points to clearly characterize the maximum loading area of the curve, which is the plateau region of the Langmuir isotherm. The sorption equilibrium for this particular actinide under these conditions may not have been attained after 24 hours of contact with the sorbent.

A second degree polynomial regression of the data, Figures 3 through 10 provides the following equations for estimating maximum loading of plutonium-239, neptunium-237 and uranium (sodium phosphate only) on these sorbents:

Plutonium-239 on GAC, $y = -9E-05x^2 + 0.037x -0.134$---------------------Figure 5

Plutonium-239 on hematite, $y = -4E-03 \ x^2 + 0.0959x$-----------------------Figure 7

Neptunium-237 on GAC, $y = -5E-05x^2 +0.04x + 0.163$---------------------Figure 6

Neptunium-237 on hematite, $y = -3E-05 \ x^2 + 0.039x – 0.303$--------------Figure 8

Neptunium-237 on sodium phosphate, $y = -38.42x^2 + 32.55x-0.130$-----Figure 9

Uranium on sodium phosphate, $y = -4.183x^2+55.584x$---------------------Figure 10

where y is loading capacity in units of μg actinide per gram of "neat" sorbent material and x is the final actinide concentration in μg/L.

Table 3 provides a summary listing of the maximum loading values for plutonium, neptunium and uranium on each of the tested solids including the mixed phase tank 50H solids. Hematite exhibited the highest loading for plutonium and neptunium of any of the solids. As expected, sodium phosphate exhibited a high affinity for uranium. The high affinity of the sodium orthophosphate for uranium was attributed to the precipitation of a uranium phosphate phase as a result of the addition of the sodium orthophosphate to the simulated waste solution.

Sodium orthophosphate did not show any measurable affinity for plutonium although it showed a significant affinity for neptunium. The affinity of these sorbents for actinides in a non caustic or neutral environment is well documented[6,7, 8]. In this study it has been shown that the precipitation of these nuclear materials from solution in the presence of these sorbents is possible. Loading capacity information provides a basis for estimating the maximum volume of nuclear waste supernatant liquid that can be transferred in and out of nuclear waste storage tanks before accumulating sufficient quantities of plutonium to pose a nuclear criticality safety concern. Conversely, the information could be used to determine how much of nuclear waste storage tank solids could be left behind and not present a safety concern due to the accumulation of fissionable materials like plutonium and neptunium.

IV. CONCLUSIONS

Loading capacity data from this study shows that solids such as granular activated carbon, hematite and sodium phosphates, if present as sludge components in nuclear waste storage tanks, are capable of precipitating/sorbing actinides like plutonium, neptunium and uranium from nuclear waste storage tank supernatant liqueur.

The loading capacity for plutonium onto granular activated carbon and iron oxide (hematite) in this type of caustic synthetic salt solution were, respectively, 3.4 (0.22) and 5.5 (0.38) µg per gram of sorbent (Numbers in bracket represent standard deviations). The loading capacity for plutonium onto typical nuclear waste storage tank sludge solid was 2.01µg per gram of sludge solids. The loading capacity for neptunium onto granular activated carbon and hematite in a caustic synthetic salt solution were, respectively, 7.9 (0.52) and >10 µg per gram of sorbent. The loading capacity for neptunium onto typical nuclear waste storage tank sludge solid was 4.48 µg per gram of sludge solid. A typical nuclear waste storage tank solid material did not show any significant affinity for uranium. Sodium phosphate showed significant affinity for both

neptunium and uranium, with loading capacities of 6.8 (0.25) and 184.6 (18.5) µg per gram of sorbent, respectively.

Based on these batch experiments the following conclusions are made:

- The removal of plutonium and neptunium from the synthetic salt solution by nuclear waste storage tank solids may be due largely to the presence of the granular activated carbon and transition metal oxides.

- Granular activated carbon and hematite show measurable affinity for both plutonium and neptunium.

- Sodium phosphate, used here as a reference sorbent for uranium, as expected, exhibited high affinity for uranium and neptunium, but failed to show any measurable affinity for plutonium.

ACKNOWLEDGEMENTS
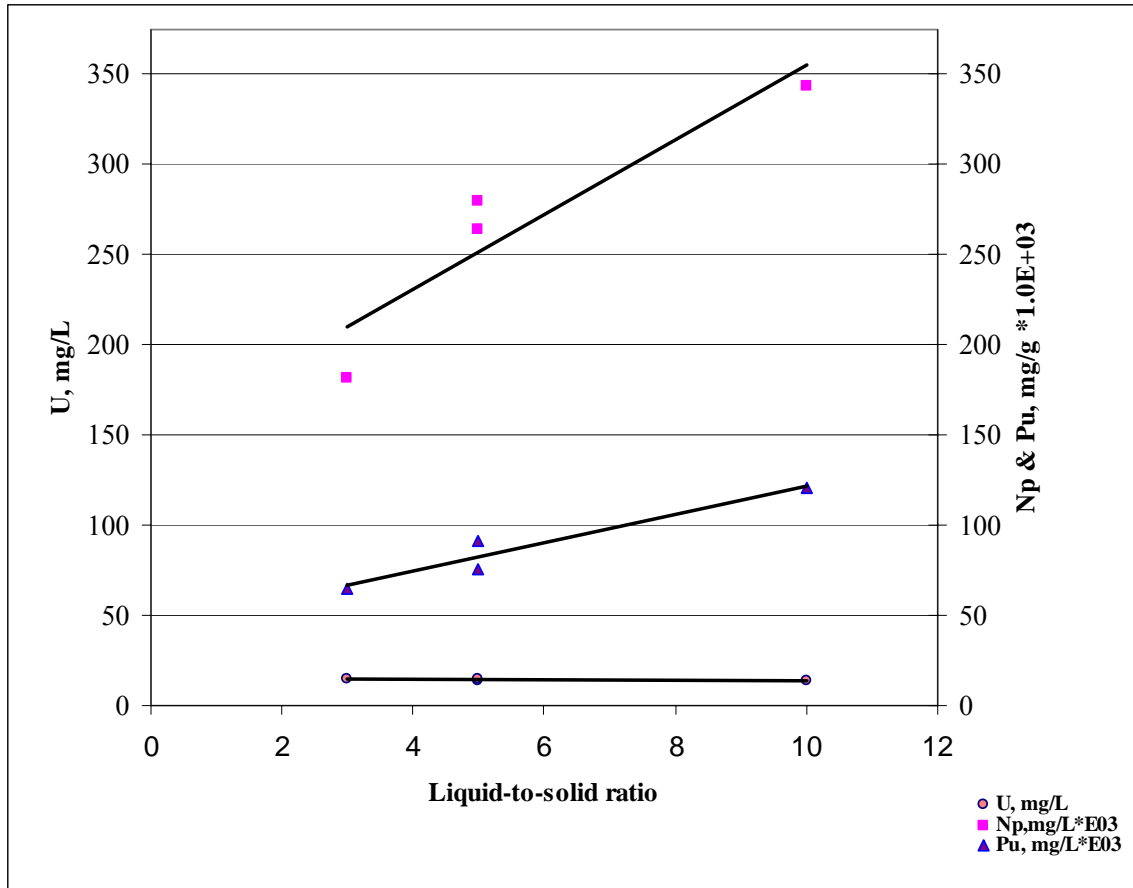
Fig.1. Plot of solution phase concentration after 24-h of contact between nuclear waste sludge solids and nuclear waste supernatant liqueur at different liquid-to-solid ratios.
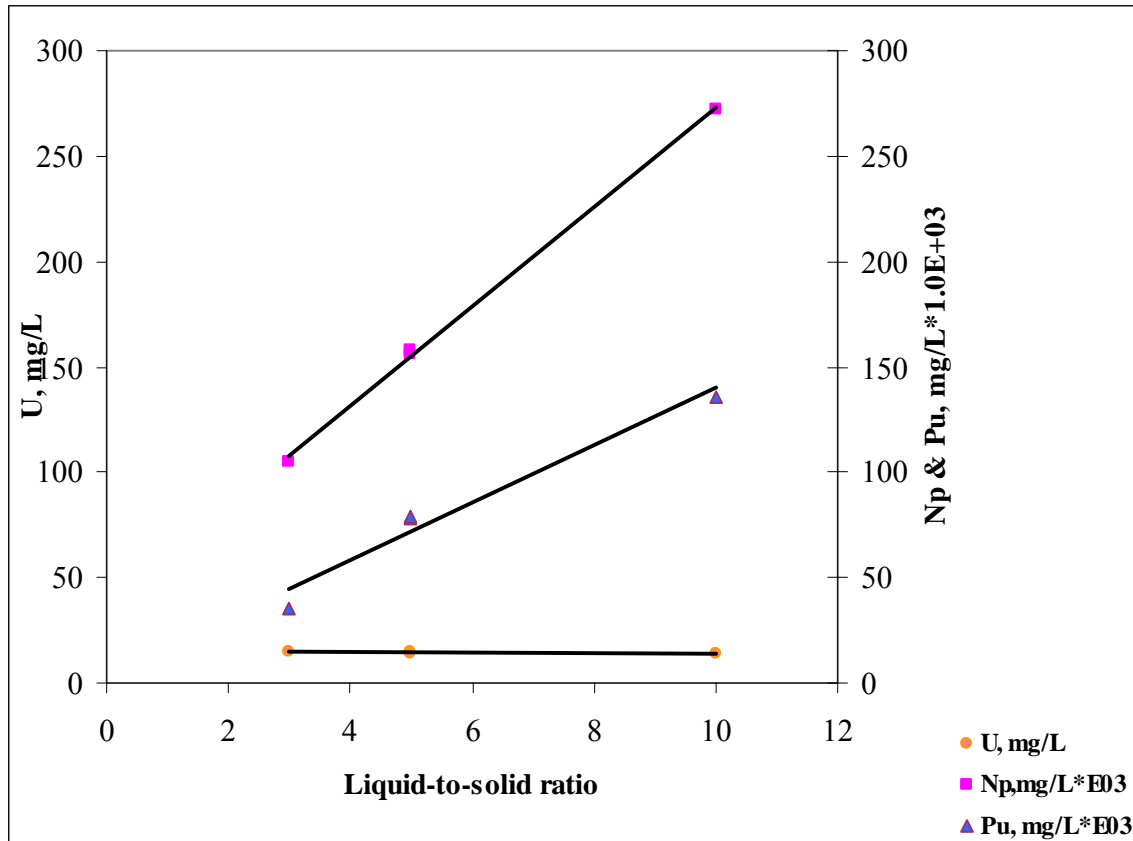
Fig.2. Plot of solution phase concentration after 24-h of contact between nuclear waste sludge solids and simulated waste solution at different liquid-to-solid ratios.
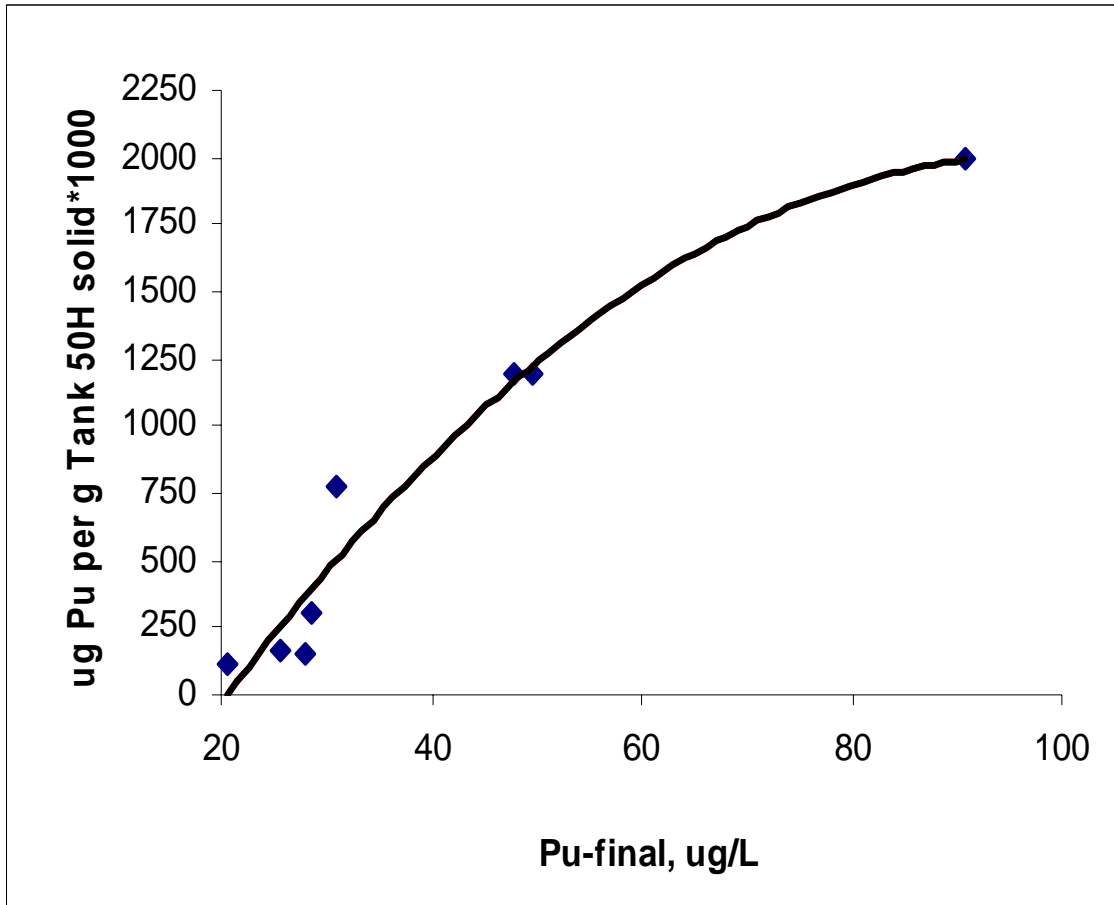
Fig.3. Plutonium sorption isotherm for nuclear waste storage tank solid in contact with tank waste supernatant liqueur.
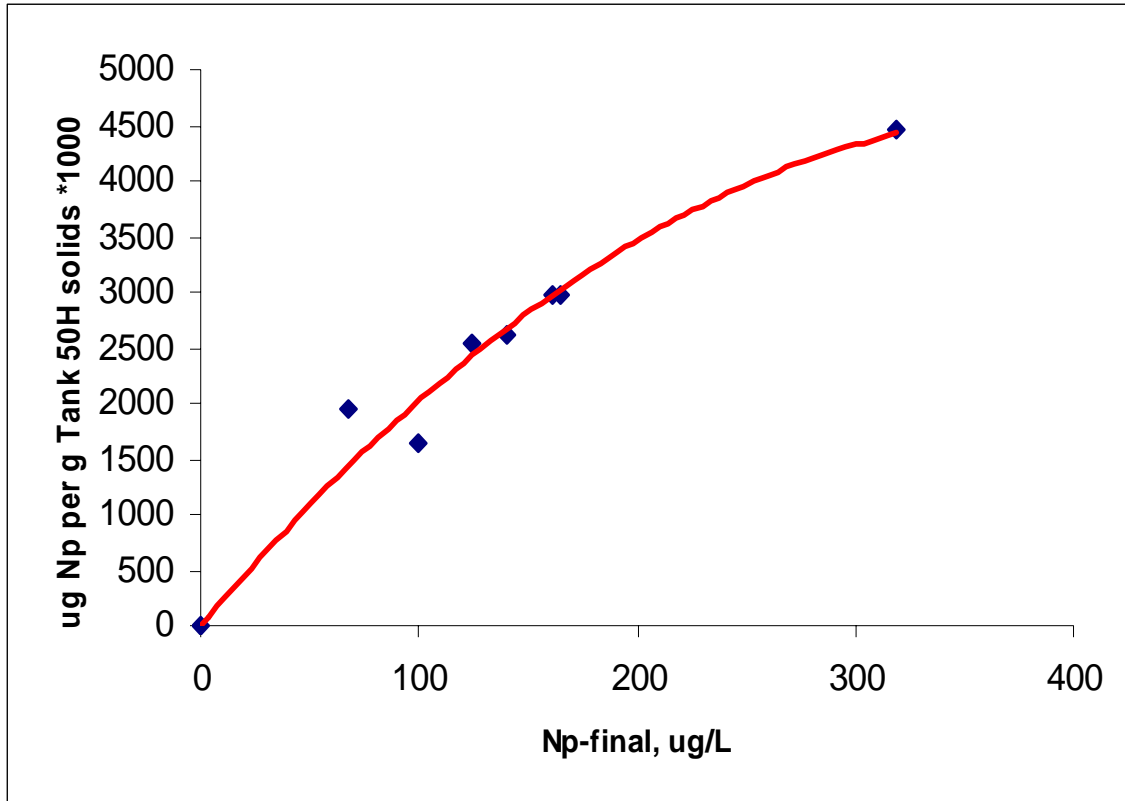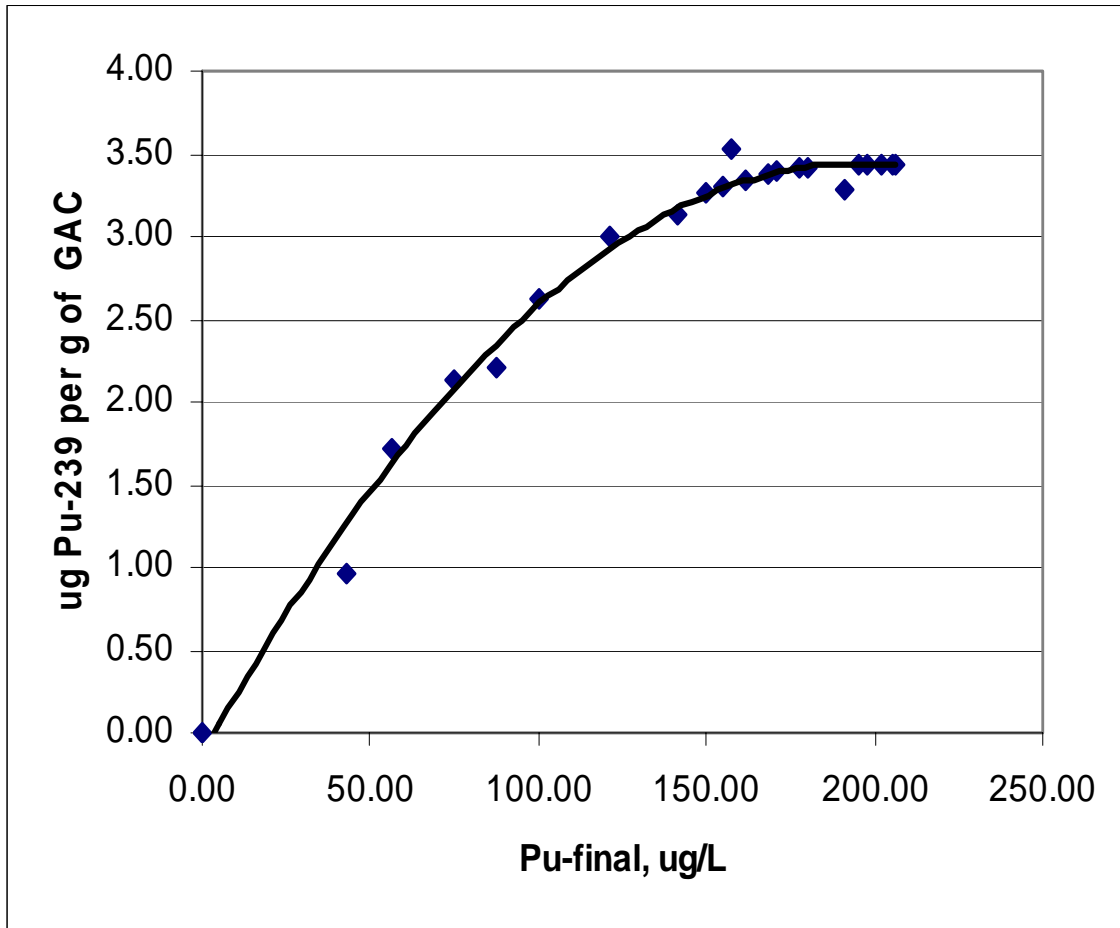
Fig.4. Neptunium sorption isotherm for nuclear waste storage tank solid in contact with tank waste supernatant liqueur.

Fig.5. Plutonium sorption isotherm for granular activated carbon in contact with simulated waste solution.
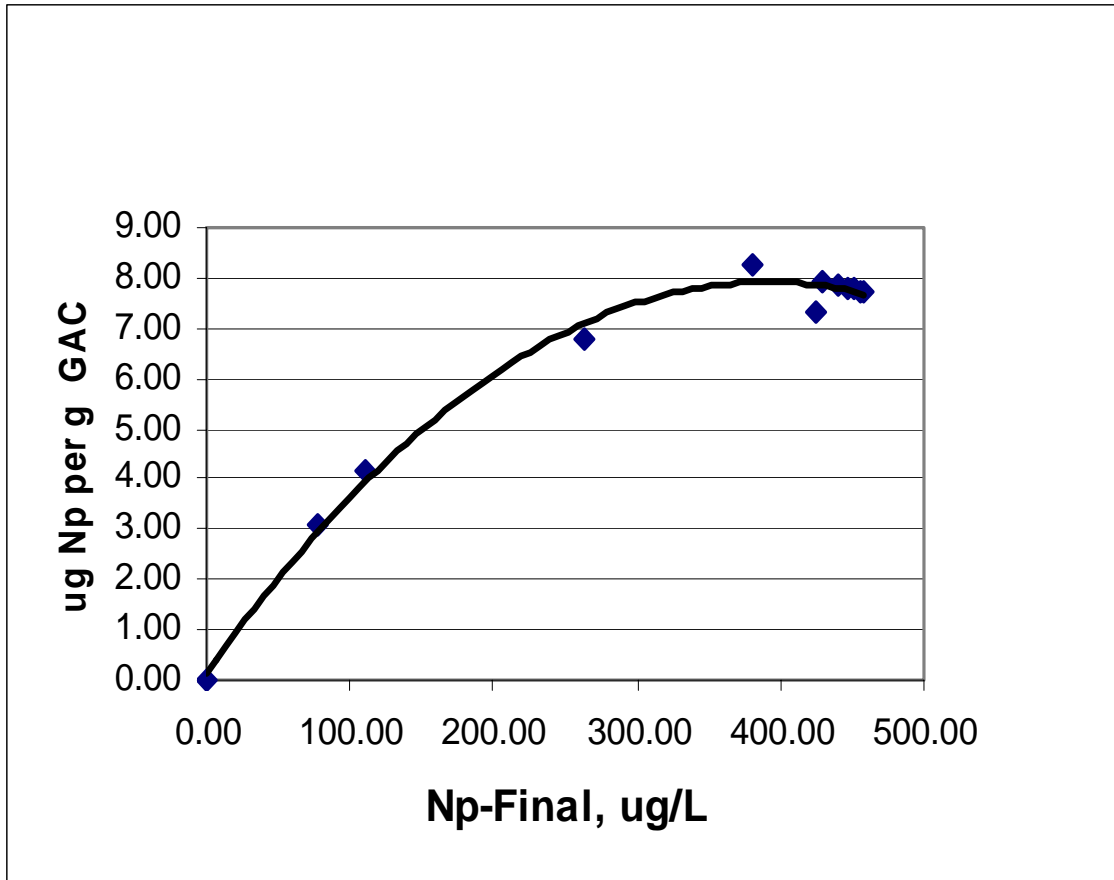
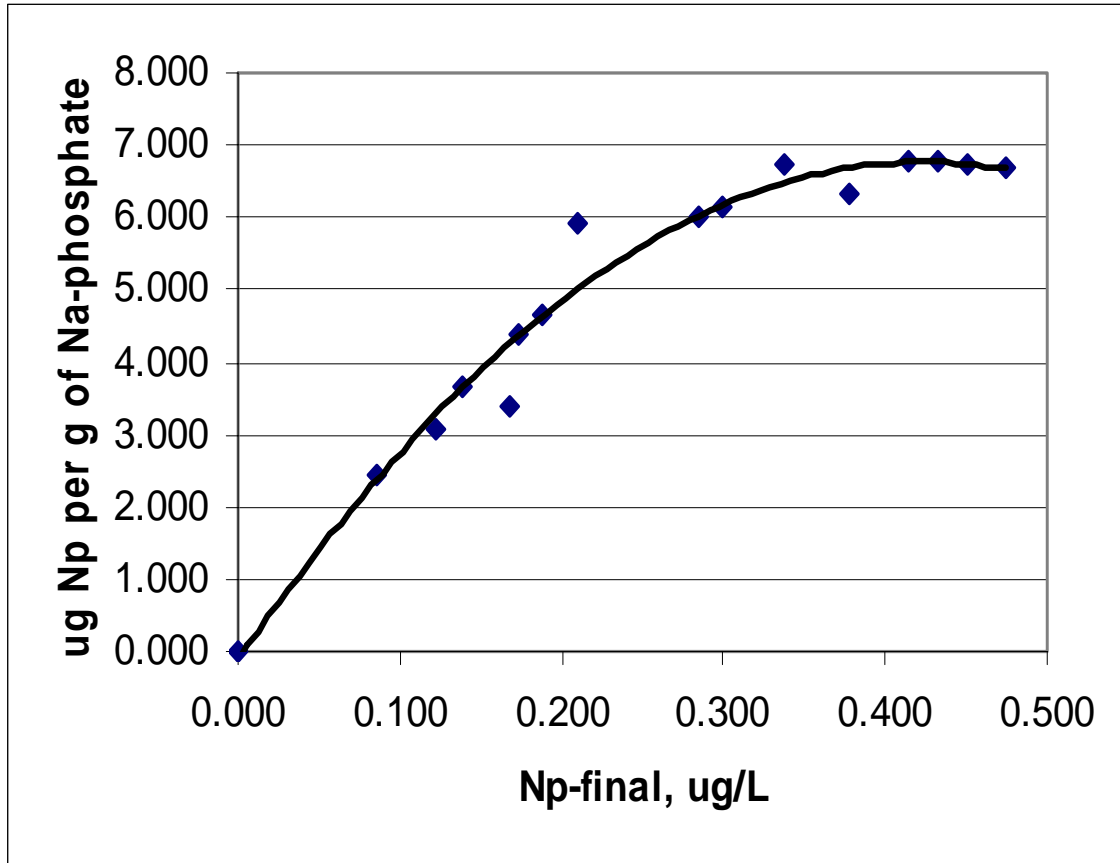Fig.6. Neptunium sorption isotherm for granular activated carbon in contact with simulated waste solution.
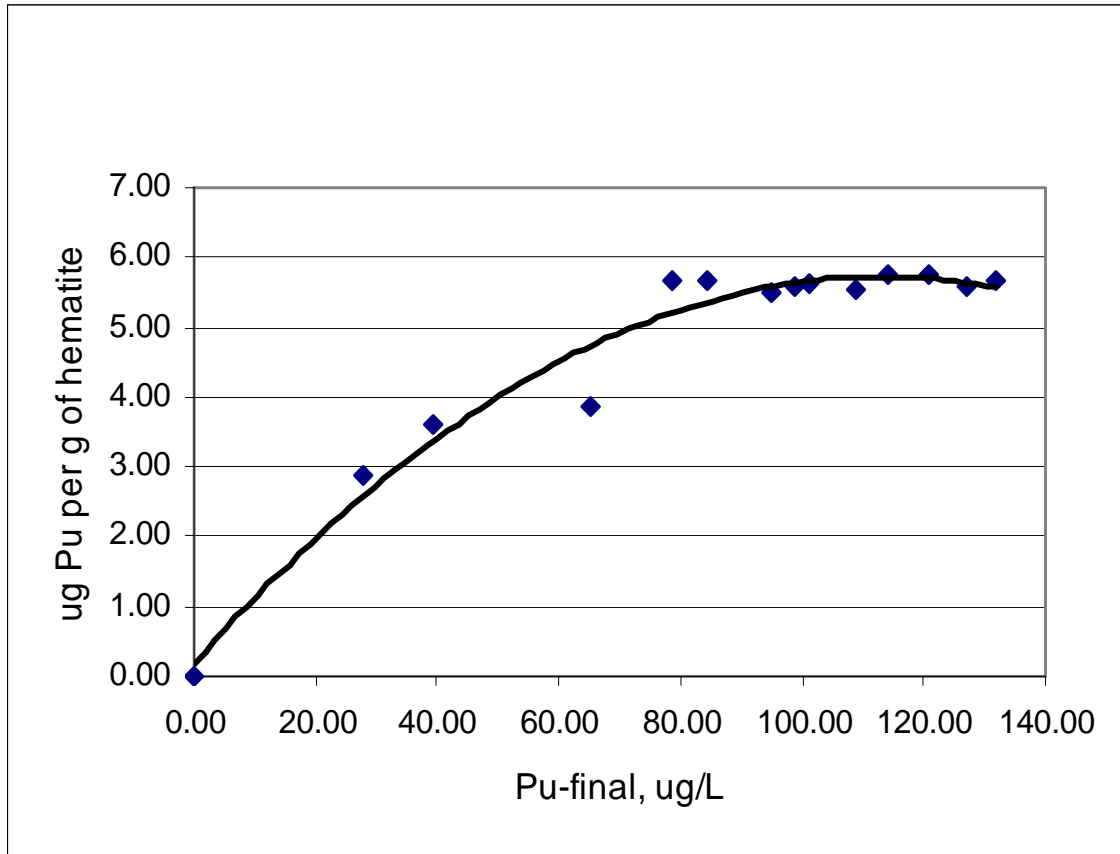
Fig.7. Plutonium sorption isotherm for hematite in contact with simulated waste solution.
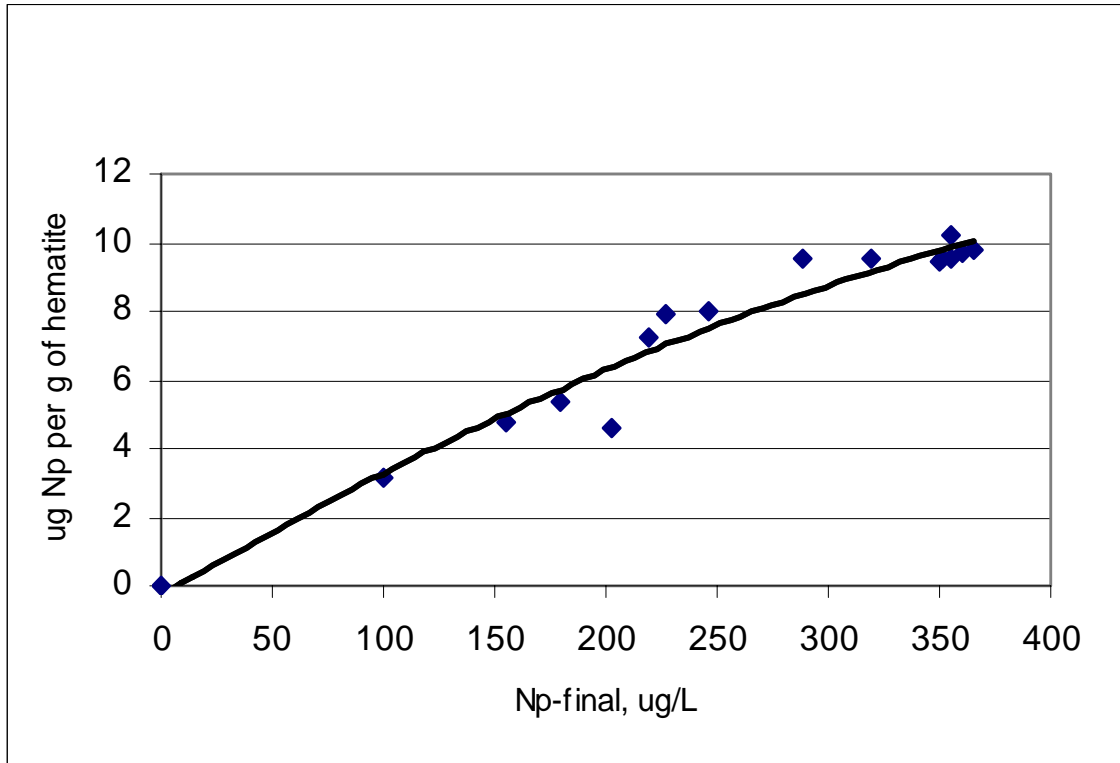
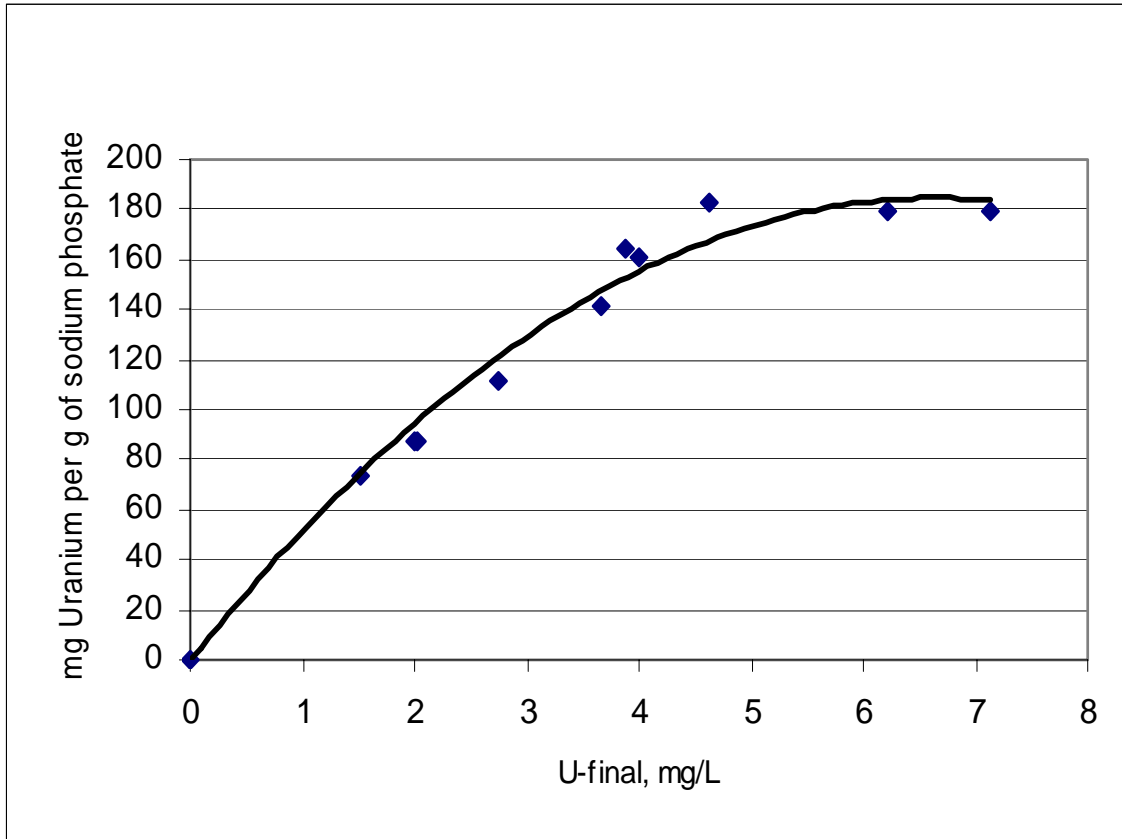Fig.8. Neptunium sorption isotherm for hematite in contact with simulated waste solution.

Fig.9. Neptunium sorption isotherm for sodium orthophosphate in contact with simulated waste solution.

Fig.10. Uranium sorption isotherm for sodium orthophosphate in contact with simulated waste solution.

Table 1. Spiked synthetic salt solution composition

Component	Concentration, M
Total Na	5.60
Free NaOH	1.33 E+00
$NaNO_3$	2.60E+00
$NaNO_2$	1.64E-01
Na_2SO_4	5.21E-01
Na_2CO_3	2.60E-02
$NaAl(OH)_4$	4.29E-01
	Mg/L
Total uranium	10.0 $\pm$1
Total plutonium	0.20 $\pm$ 0.02
Neptunium-237	0.50 $\pm$ 0.050

Table 2. Real waste supernatant composition

Component	Concentration	Units
Na	9.16	M
K	0.06	M
Ag	9.46	mg/L
Ba	2.82	mg/L
Ca	19.92	mg/L
Cd	2.16	mg/L
Cr	64	mg/L
Mo	78	mg/L
Free OH^-	6.81	M
NO_3-	0.95	M
NO_2^-	0.68	M
AlO_2^-	0.30	M
SO_4^{2-}	0.07	M
CO_3^{2-}	0.11	M
PO_4^{3-}	0.01	M
Total Uranium	19 ± 1	mg/L
Total Plutonium	150 ± 5	μg/L
Neptunium-237	650	μg/L

Table 3. Measured loading capacities for plutonium, neptunium and uranium onto solids.

Sorbents	Maximum Pu loading μg/g solid	Maximum Np loading μg/g solid	Maximum U loading μg/g solid
Tank 50H solids	**2.01**	**4.48**	**NA**
Granular activated carbon	**3.4** (0.22)*	**7.9** (0.52)	**NA**
Hematite	**5.5** (0.38)	**>10**	**NA**
Sodium orthophosphate	**Not measured**	**6.8** (0.25)	**184.6** (18.5)

NA = No measurable absorption of uranium.
* Numbers in bracket represent standard deviations.

LIST OF FIGURES

LIST OF TABLES

[1] Wilmarth, W.R., "Results of Sample Analysis from Solids Removed from Tank 50H", Report. WSRC-TR-2002-00506, November 1, 2002.

[2] Oji l. N. and Hobbs D. T., "Evaluation of the Effects of Tank 50H Solids on Dissolved Uranium, Plutonium and Neptunium", Report. WSRC-RP-2003-00224, Rev. 0, April 17, 2003.

[3] J. L. Means, D. A. Crerar, M. P. Borscsik and J. O. Duguid, "Adsorption of Co and selected actinides by Mn and Fe oxides in soils and sediments," *Geochim. Cosmochim. Acta*, *42, 1763-1773 (1978).*

[4] M. Kohler, B. D. Honeyman and J. O. Leckie "Neptunium (V) sorption on hematite (α-Fe_2O_3) in aqueous suspension: the effect of CO_2," *Radiochim. Acta 85, 33-48 (1999).*

[5] S. Nagasaki, S. Tanaka and A. Suzuki, "Influence of Fe (III) colloids on Np (V) migration through quartz-packed columns," *Journal of Nuclear Science Technology*, 31(2), pp 143-*150 (Feb. 1994).*

[6] Nagasaki, S.; Tanaka, S; Suzuki, A.; Influence of Fe (III) colloids on Np(V) migration through quartz-packed columns. *Journal of Nuclear Science Technology*, 1994, 31(2), 143-150.

[7] Kohler,M.; Honeyman, B. D.; Leckie, J. O.; Neptunium (V) sorption on hematite (α-Fe_2O_3) in aqueous suspension: the effect of CO_2. *Radiochim. Acta* 1999, 85, 33-48.

[8] Means, J. L.; Crerar, D. A.; Borscsik, M.P.; Duguid, J. O.; Adsorption of Co and selected actinides by Mn and Fe oxides in soils and sediments. *Geochim. Cosmochim. Acta*; 1978, 42, 1763-1773.