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Uranium and Plutonium Loading onto Monosodium Titanate (MST) in Tank 50H

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AUGUST 2006

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REVIEWS AND APPROVALS

8/23/06

D. T. Hobbs, Author, Process Chemistry and Science — Date

8.23.06

F. F. Fondeur, Reviewer, Process Chemistry and Science — Date

8/23/06

S. D. Fink, Manager, Manager, Process Chemistry and Science — Date

8/28/06

D. T. Conrad, Manager, Salt Processing Design Authority / T48 Disposition — Date

8/3./06

D. J. Martin, Manager, TF Process Engineering — Date

8/25/06

J. C. Griffin, Manager, Chemical Science and Technology — Date

Summary
A possible disposition pathway for the residue from the abandoned In-Tank Precipitation (ITP) sends the material from Tank 48H in increments to Saltstone via aggregation in Tank 50H. After entering Tank 50H, the amount of fissile material sorbed on MST may increase as a result of contacting waste solutions with dissolved uranium and plutonium. SRNL recommends that nuclear criticality safety evaluations use uranium and plutonium loadings onto MST of 14.0 $\pm$ 1.04 weight percent (wt %) for uranium and 2.79 $\pm$ 0.197 wt % for plutonium given the assumed streams defined in this report. These values derive from recently measured for conditions relevant to the Actinide Removal Process (ARP) and serve as conservative upper bounds for uranium and plutonium loadings during the proposed transfers of MST from Tank 48H into Tank 50H.

Introduction
Tank 48H contains tetraphenylborate solids and MST from the abandoned ITP process. A possible disposition pathway sends this material to Saltstone in increments via aggregation in Tank 50H. Upon entering Tank 50H, the MST will contact fresh waste and aggregating solutions that contain dissolved uranium and plutonium. This contact could lead to sorption of additional uranium and plutonium onto the MST. Closure Business Unit requested SRNL to evaluate conditions during aggregation in Tank 50H and recommend bounding loading values for uranium and plutonium on MST.[1]

Discussion
An earlier (2002) estimate of the maximum loadings of uranium and plutonium on MST in Tank 48H reported values of 0.49 wt % for uranium and 0.0049 wt % for plutonium.[2] Given the length of time that the MST has been in contact with the supernate in Tank 48H (>10 years), this evaluation assumes that the MST is in chemical equilibrium with respect to adsorption of uranium and plutonium onto MST. This assumption appears valid since there have been no addition of supernates into Tank 48H since 1995 and analyses over the period of 1997 – 2003 indicated no changes in the concentrations of uranium and neptunium in filtered Tank 48H supernate samples.[3]

Note that plutonium measurements indicated that the concentrations of plutonium in the filtrate samples may have decreased as the more recent 2003 samples reported values for ^{239}Pu of <5.00E-4 and <2E-03 compared to the 1995 result of 2.87E-03. However, the analysis of the 2003 samples included different sample preparation protocols that resulted in diluting the plutonium below quantifiable limits. Thus, we cannot conclusively determine if the concentration of plutonium changed during this time period. If the plutonium concentrations indeed decreased, the maximum amount of plutonium that could have adsorbed is only 2.6 grams, which would increase the estimated loading of plutonium onto MST in Tank 48H from 0.0049 wt % to 0.0050 wt %.

[1] "Develop MST Maximum Loading of Fissile Material," Technical Task Request, SP-TTR-20006-00004, Revision 0, March 15, 2006.
[2] "Estimated Maximum Loading of Uranium and ^{239}Pu on Monosodium Titanate Presently Stored in Tank 48H," memo from D. T. Hobbs to S. D. Fink, SRT-LWP-2002-00112, Rev. 0.
[3] "Analysis of Tank 48H Samples HTF-E-03-73 (June 03, 2003) and HTF-E-03-127 (September 17, 2003), WSRC-TR-2003-00720, Rev. 0, January 20, 2004.

Upon transfer into Tank 50H, the MST will contact supernates and aggregating solutions with dissolved concentrations of uranium and plutonium that differ from those in the Tank 48H supernate. Thus, the MST could adsorb additional uranium and plutonium if the dissolved concentrations of uranium and plutonium in Tank 50H exceeds that in Tank 48H. Ketusky recently reviewed conditions in Tank 48H and the planned flowsheet for disposition of Tank 48H through Tank 50H.[4] He concluded that the supernate in Tank 48H contains a maximum of 9.2 mg L^{-1} uranium and 0.281 mg L^{-1} plutonium. Furthermore, he reported that the supernates in Tank 50H will contain a maximum of 6.5 mg L^{-1} of uranium and 0.033 mg L^{-1} of plutonium. Since the maximum expected concentrations of uranium and plutonium in Tank 50H are less than that presently in Tank 48H, there is no chemical driving force for additional adsorption. Thus, no additional adsorption of uranium and plutonium is expected.

Given uncertainties in the dissolved concentrations of uranium and plutonium in waste supernates and the possibility of changes in supernate transfers into Tank 50H, there may be instances when the uranium and plutonium concentrations in the Tank 50H supernates may exceed that estimated for the supernate presently in equilibrium with the MST in Tank 48H. In those instances some adsorption of uranium and plutonium could occur resulting in increased loadings onto the MST. To allow for possible higher uranium and plutonium concentrations that could lead to additional adsorption of actinides, SRNL recommends using the higher loading values of 14.0 $\pm$ 1.04 wt % for uranium and 2.79 $\pm$ 0.197 wt % for plutonium. These loading values are 29 and 570 times greater than the presently estimated loadings of uranium and plutonium, respectively, for the MST presently stored in Tank 48H and, thus, provide conservative upper bounds for the adsorption of uranium and plutonium onto MST during disposition of Tank 48H material through Tank 50H.

Note, that the affinity of the MST presently stored in Tank 48H to adsorb uranium and plutonium is likely to have decreased over that of fresh MST due to the age of the material (>10 years) and the presence of tetraphenylborate solids. For this evaluation SRNL assumes that aging and presence of tetraphenylborate solids do not alter the adsorption of uranium and plutonium onto the MST upon contact with fresh supernates in Tank 50H. This assumption provides additional conservatism to the recommended loading values, which were determined with fresh MST.

The quantity of uranium and plutonium that will adsorb onto MST depends on the chemical driving force. The driving force varies with (i) the concentrations of uranium and plutonium, (ii) the ratio of supernate to MST solids and (iii) temperature. Of these three factors, previous testing demonstrated that temperature plays a minor role, if any, in the adsorption of uranium and plutonium onto MST.[5] For example, temperature was not a statistically significant factor for uranium loading over the temperature range from 25 to 65 •C

[4] "Engineering Study: Determination of Inputs to Monosodium Titanate (MST) Adsorption Modeling of Uranium/Plutonium (U/Pu) in Tanks 48/50 During Aggregation," Ketusky, E. T., CBU-PIT-2006-00062, Rev. 1, June 28, 2006.

[5] "Final Report on Phase III Testing of Monosodium Adsorption Kinetics," Hobbs, D. T.; Bronikowski, M. G.; Edwards, T. B.; Pulmano, R. L.; Technical Report, Washington Savannah River Company, WSRC-TR-99-00134, Rev. 0, May 28, 1999.

(see Table X in reference 5). For plutonium, loadings decreased slightly with increased temperature (see Table X in reference 5).

The maximum temperature that could occur in Tank 50H during aggregation is reported at 40 •C. Since the temperature in Tank 50H will not exceed the maximum tested temperature (65 •C), the effects of temperature are bounded by previous testing. Uranium and plutonium loadings measured in the ARP testing occurred at 25 $\pm$ 3 •C. Given the minor effect, if any, and the small temperature difference between 25 •C and 40 •C, the loadings measured in the ARP testing would not be significantly different at 40 •C.

The second parameter that influences the degree of adsorption is the concentration of uranium and plutonium in the supernate that contacts the MST. The recommended values for uranium and plutonium loading (14.0 $\pm$ 1.4 wt % for uranium and 2.79 $\pm$ 0.197 wt % for plutonium) were measured using a simulant that featured much higher uranium and plutonium concentrations than the maximum values estimated to occur in Tank 50H during the disposition of the Tank 48H material via aggregation. For example, the uranium and plutonium concentrations in the simulated waste solution measured 26.5 $\pm$ 5.3 mg L^{-1} in uranium and 0.882 $\pm$ 0.0946 mg L^{-1} in plutonium[6] compared to the estimated maximum concentrations in Tank 50H of 6.5 mg L^{-1} for uranium and 0.033 mg L^{-1} for plutonium. Given that the estimated maximum uranium and plutonium concentrations in Tank 50H are much lower than the high actinide simulant reported above and also below that for the supernate presently in contact with the MST, the recommended loading values are conservative upper bounds for the loading of uranium and plutonium onto MST upon transfer into Tank 50H.

The third parameter that influences the degree of adsorption is the ratio of the volume of supernate to the mass of MST (referred to as the phase ratio). In general, loading increases with an increase in the phase ratio. Disposition of the Tank 48H material will transfer varying quantities of MST into Tank 50H and contact supernates that also transfer into Tank 50H during the same time. The quantity of MST in Tank 50H at any point in time varies based on the quantity of material transferred from Tank 48H and that transferred out of Tank 50H to Saltstone. Phase ratios used for much of the testing in support of salt processing falls in the range 0.5 – 5.0 L g^{-1}.[7,8,9,10] The recent Actinide Removal Process (ARP) testing used a phase ratio of 42.5 to measure uranium and plutonium loadings.

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[6] "Determination of Fissile Loadings onto Monosodium Titanate (MST) under Conditions Relevant to the Actinide Removal Process Facility," Peters, T.B.; Hobbs, D. T.; Fink, S. D.; Technical Report, Washington Savannah River Company, WSRC-TR-2005-00514, Rev. 0, November 15, 2005.

[7] "Phase IV Testing of Monosodium Titanate Adsorption with Radioactive Waste," Hobbs, D. T.; Pulmano, R. L.; Technical Report, Westinghouse Savannah River Company, WSRC-TR-99-00286, Rev. 0, September 3, 1999.

[8] "Phase IV Simulant Testing of Monosodium Titanate Adsorption Kinetics," Hobbs, D. T.; Pulmano, R. L.; Technical Report, Westinghouse Savannah River Company, WSRC-TR-99-00219, June 29, 1999.

[9] "Phase V Simulant Testing of Monosodium Titanate Adsorption Kinetics," Hobbs, D. T.; Blume, M. S.; Thacker, H. L., Technical Report, Westinghouse Savannah River Company, WSRC-TR-2000-00142, Rev. 0, May 24, 2000.

[10] "Screening Evaluation of Alternate Sorbents and Methods for Strontium and Actinide Removal from Alkaline Salt Solution," Hobbs, D. T.; Blume, M. S.; Thacker, H. L.; Technical Report, Westinghouse Savannah River Company, WSRC-TR-2001-00072, Rev. 0, February 2001.

Phase ratios within Tank 50H will likely be well within the range of 0.5 to 42.5 L g^{-1}. However, there may be times in which the phase ratio in Tank 50H could exceed that tested in the laboratory. Since the uranium and plutonium concentrations are such that there is little or no chemical driving force for adsorption, the increased phase ratios, if present, would not be expected to significantly increase loading. The additional loading, if it occurs, would be well within the difference in the estimated current MST loadings in Tank 48H (0.49 wt % for uranium and 0.0049 wt % for plutonium) and the recommended values for use in evaluating nuclear safety (14.0 $\pm$ 1.4 wt % for uranium and 2.79 $\pm$ 0.197 wt % for plutonium). Thus, the recommended loadings provide a conservative margin of safety to accommodate higher phase ratios, if present, in Tank 50H.