Fate of Fissile Material Bound to Monosodium Titanate (MST) During Copper Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Waste

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EXECUTIVE SUMMARY

At the Savannah River Site (SRS), Tank 48H currently holds approximately 240,000 gallons of slurry which contains potassium and cesium tetraphenylborate (TPB). A copper catalyzed peroxide oxidation (CCPO) reaction is currently being examined as a method for destroying the TPB present in Tank 48H. Part of the development of that process includes an examination of the fate of the Tank 48H fissile material which is adsorbed onto monosodium titanate (MST) particles. This report details results from experiments designed to examine the potential degradation of MST during CCPO processing and the subsequent fate of the adsorbed fissile material.

Experiments were conducted to simulate the CCPO process on MST solids loaded with sorbates in a simplified Tank 48H simulant. Loaded MST solids were placed into the Tank 48H simplified simulant without TPB, and the experiments were then carried through acid addition (pH adjustment to 11), peroxide addition, holding at temperature (50 °C) for one week, and finally NaOH addition to bring the free hydroxide concentration to a target concentration of 1 M. Testing was conducted without TPB to show the maximum possible impact on MST since the competing oxidation of TPB with peroxide was absent. In addition, the Cu catalyst was also omitted, which will maximize the interaction of H_2O_2 with the MST; however, the results may be non-conservative assuming the Cu-peroxide active intermediate is more reactive than the peroxide radical itself.

The study found that both U and Pu desorb from the MST when the peroxide addition begins, although to different extents. Virtually all of the U goes into solution at the beginning of the peroxide addition, whereas Pu reaches a maximum of ~34% leached during the peroxide addition. Ti from the MST was also found to come into solution during the peroxide addition. Therefore, Ti is present with the fissile in solution.

After the peroxide addition is complete, the Pu and Ti are found to precipitate from solution, while the U remains in solution throughout the remaining processes, including pH adjustment to 1 M free hydroxide. The Ti is likely forming a peroxotitanate material, which can then resorb the leached Pu from solution, but has a low affinity for U. Since Pu was not detected in the SEM-EDS studies, it cannot be conclusively determined in what form the Pu returns to the solids; however, the Pu likely resorbed onto the peroxotitanate material.

Based on the results of this experiment, Savannah River National Laboratory (SRNL) recommends the following experiments to further examine the fate of fissile material in CCPO processing of Tank 48H.

- Repeat with full simulant matrix (organic and Cu catalyst present along with simulated radioactive sludge).
- Repeat of the above test after selection of final conditions (i.e., pH, temperature) if they differ from conditions tested.

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LIST OF ABBREVIATIONS

CCPO	copper catalyzed peroxide oxidation
DWPF	Defense Waste Processing Facility
FBSR	Fluidized Bed Steam Reforming
HLW	High Level Waste
ICP-ES	inductively coupled plasma – emission spectroscopy
ICP-MS	inductively coupled plasma – mass spectroscopy
ITP	In Tank Precipitation
mMST	modified monosodium titanate
MST	monosodium titanate
NaTPB	sodium tetraphenylborate
PUREX	Plutonium/Uranium Extraction
PuTTA	plutonium thenoyltrifluoroacetone scintillation
PXRD	powder X-ray diffraction
SEM-EDS	scanning electron microscopy – energy dispersive spectroscopy
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation, LLC
SRS	Savannah River Site
TPB	tetraphenylborate
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request

1.0 Introduction

At SRS, Tank 48H currently holds approximately 240,000 gallons of slurry which contains potassium and cesium tetraphenylborate. Original plans called for processing this TPB slurry in the In Tank Precipitation (ITP) Facility, the Late Wash Facility, and the Defense Waste Processing Facility (DWPF) Salt Cell. That process scheme included concentrating the TPB, washing the non-radioactive salts to reduce the nitrite concentration, decomposing the TPB to benzene, and separating the benzene from the aqueous waste. However, these facilities ceased operation due to high benzene generation during startup of the ITP Facility.

In 2001, a team evaluated processing options, which would return Tank 48H to routine High Level Waste (HLW) service.[1] The team used the Systems Engineering approach to evaluate the alternatives and make a recommendation to management. The group evaluated 40 options which were subsequently reduced to 15. A task plan[2] detailed the experimental evaluation of these processing options using simple, laboratory scale testing with simulants. Most of the processing focused on three possible decomposition schemes: namely, catalysts, oxidants, and acids.

In June 2009, Fluidized Bed Steam Reforming (FBSR) was designated the technology to remediate Tank 48H.[3] Work proceeded until June 2011, when the work was put in suspension until the previous work on decomposition using catalysts, oxidants, and acids could be re-evaluated and re-examined for cost effectiveness.[4]

A CCPO process is currently being examined as a method for destroying the TPB present in Tank 48H. In addition to the TPB, Tank 48H also contains monosodium titanate (MST) that was added during the ITP process to sorb soluble Sr and actinides. Part of the development of the CCPO process includes an examination of the fate of the fissile material during processing. This report details results of experiments designed to examine the fate of the fissile material on the MST currently present in Tank 48H.

This work was performed at the request of Savannah River Remediation, LLC (SRR)[5] and was controlled by a Task Technical and Quality Assurance Plan (TTQAP).[6] This report covers only a portion of the work detailed in the referenced Technical Task Request (TTR) and TTQAP. Results from the remaining tasks will be detailed in separate reports.

2.0 Experimental Procedure

2.1 Materials

The MST used in these studies was prepared using a sol-gel process developed at SRNL and supplied by Optima Chemical Group LLC (Douglas, GA, Lot #00-QAB-417) as a 15 wt % suspension in water containing 0.10-0.15 M NaOH and 100-150 mg L^{-1} NaNO$_2$.[7]

2.2 Tank 48H Simulant

A simplified Tank 48H simulant solution was prepared following the standard recipe,[8] omitting the solids and organics. Specifically the following components were omitted: sodium tetraphenylborate (NaTBP), Plutonium/Uranium Extraction (PUREX) sludge simulant, MST, biphenyl, diphenyl mercury, and benzene. The composition is shown in Table 2-1 excluding trace metals present at concentrations less than 0.001 M.

Table 2-1. Composition of Tank 48H Simplified Simulant

Component	Target Concentration (M)
Na^+	3.262
OH^-	1.633
NO_2^-	0.468
NO_3^-	0.215
CO_3^{2-}	0.455
AlO_2^-	0.073
PO_4^{3-}	0.005
SO_4^{2-}	0.003
Cl^-	0.003
F^-	0.001
K^+	0.064
Si	0.003
phenol	0.010

2.3 Loading of MST

Samples of MST were loaded with sorbates (Sr, Pu, Np, and U) by contacting with a simulated waste solution for 1 week. The composition of the simulated waste solution (SWS-9-2009) is provided in Table 2-2. The simulant had been prepared previously, and was spiked with ^{85}Sr just prior to use in this testing. Three loadings were performed by adding 2.345 g of a 14.71 wt % suspension (0.34 g MST) of MST to three 1-L bottles. 860 mL of SWS-9-2009 was then added to each bottle, and the bottles were stirred at room temperature for 1 week. The final sorbate loadings on the MST were determined by analyzing aliquots of the supernate from each bottle by gamma spectroscopy, plutonium thenoyltrifluoroacetone scintillation (Pu TTA), and inductively coupled plasma – mass spectroscopy (ICP-MS) at the end of the 1 week loading period.

Table 2-2. Composition of SWS-9-2009

Component	Measured Concentration
Free NaOH	1.27 M
Total $NaNO_3$	2.10 M
$NaAl(OH)_4$	0.389 M
$NaNO_2$	0.125 M
Na_2SO_4	0.508 M
Na_2CO_3	0.030 M
Total Na	5.05 M
^{85}Sr	2.43E+04 dpm/mL
Total Sr	0.214 mg/L
^{137}Cs	1.14E+05 dpm/mL
Total Cs	17.9 mg/L
Pu	142 µg/L
Np	516 µg/L
U	10,900 µg/L

2.4 Simulated Tank 48H Processing

A total of three tests were performed with the loaded MST. Tests #2 and 3 (duplicates) were subjected to the following sequential process conditions: acid addition, temperature increase to 50 °C, peroxide addition at 50 °C, and NaOH addition at room temperature to adjust the solution

to 1 M free hydroxide. A control test (Test #1) was subjected to each step except that during the 50 °C hold no peroxide was added.

Two hundred milliliters of the Tank 48H simplified simulant were added to each of three 500-mL polyethylene bottles. Each of the MST loading bottles (see Section 2.3) was then filtered through a 0.45-µm filter to collect the loaded MST. The solids were washed briefly with a few mL of Tank 48H simplified simulant. After washing, the MST was transferred to the test bottle by using aliquots of the solution in the test bottle to slurry and transfer the solids from the filter. The time the solids were added was recorded as the start time. A sample was also removed at this point. The test bottles were then transferred to a 25 °C shaker oven and were shaken at 175 rpm. A sample was not taken after briefly washing the loaded solids, as leaching of any sorbates was expected to be minimal. This was confirmed from analysis of the sample taken after the loaded solids were added to the simplified simulant (t = 0 sample).

Three 60-mL syringes were then filled with 35 mL of 50 wt % HNO_3 and were loaded into a syringe pump. Tubing was connected from the syringes to the tops of the test bottles. The 50 wt % HNO_3 was then added to the test bottles at a rate of 1.5 mL per hour. This rate was selected to require approximately 24 hours for the acid addition to complete; however, this is much slower than the acid addition rate used in the Tank 48H simulant testing (i.e., ~3.6 % of that rate).[9] The start time of the acid addition was recorded. After approximately 19 hours of acid addition, the pH of the test bottles was measured with a portable pH meter. The pH was measured to be 11.9. Acid addition was continued, and the pH was checked hourly, until a pH below 11 was reached. Once a pH of below 11 was reached, the acid addition was stopped. Approximately 32 mL of 50 wt % HNO_3 had been added to reach the end point. The final pH of each test bottle was recorded, and a sample was removed. After sampling, the test bottles were returned to the shaker oven, and the temperature was increased to 50 °C.

Two 60-mL syringes were then filled with 50 wt % H_2O_2 and were loaded into the syringe pump. Tubing was connected from the syringes to Test bottles #2 and #3. Test bottle #1 is a control and did not receive any H_2O_2. The peroxide addition was then started at a rate of 0.32 mL/h, and was then increased to 0.4 mL/h 50 minutes later. The rate was selected to add the same scaled volume of H_2O_2 added in the 2005 demonstration over a time period of 1 week (i.e., a ~6X accelerated rate).[10] The accelerated peroxide addition rate is non-conservative with respect to increasing the reaction with MST due to the rate of auto-decomposition of hydrogen peroxide in alkaline media, which increases with increasing peroxide concentration.[11] The peroxide addition continued for 1 week, until a total of 67.2 mL of 50 wt % H_2O_2 had been added to each bottle. Samples were removed at the following times during the H_2O_2 addition: 1 day, 2 days, 3 days, 6 days, and 7 days after peroxide addition began. After the peroxide addition was complete, the test bottles continued to shake at 50 °C for 1 week, and two additional samples were removed (8 days and 14 days after peroxide addition began).

After the one week hold at 50 °C, the oven temperature was reduced to 25 °C. After the test bottles had cooled to room temperature, the final pH was measured. Aliquots of 50 wt % NaOH were then added to bring the free hydroxide concentration to a target concentration of 1 M. After adding the NaOH, the test bottles were shaken overnight. The test bottles were then filtered, and samples of the filtrate were removed for analysis. After air drying, samples of the solids were also submitted for analysis.

2.5 <u>Sample Analysis</u>

Filtrate samples were removed periodically and analyzed using inductively coupled plasma – emission spectroscopy (ICP-ES), ICP-MS, gamma scan analysis, and PuTTA.   Prior to

submission, the samples were filtered through a 0.1-µm syringe filter and were acidified with an equal volume of 5 M HNO_3.

Samples of the solids collected at the end of the testing were submitted for powder X-ray diffraction (PXRD) and scanning electron microscopy – energy dispersive spectroscopy (SEM-EDS) analyses. In addition, samples of the solids were dissolved in concentrated H_2SO_4 and were analyzed using ICP-ES, ICP-MS, gamma scan, and PuTTA analyses.

3.0 Results and Discussion

3.1 MST Loading

Table 3-1 provides the sorbate loading values for the three samples of MST used in the testing.

Table 3-1. Sorbate Loadings on MST

	MST Sample #1	MST Sample #2	MST Sample #3
^{85}Sr (dpm/g)	6.05E+07	6.05E+07	6.07E+07
Pu (µg/g)	321	326	319
Np (µg/g)	613	678	693
U (µg/g)	7890	8740	7740

3.2 Observations

3.2.1 *pH Adjustment*

The 50 wt % nitric acid was added at a rate of 1.5 mL per hour to each of the three tests bottles. After approximately 29 mL of acid had been added, the pH of test bottle #3 was measured to be 11.89. The acid addition continued, and the pH of one bottle was measured every hour for the next 4 hours. The pH was found to slowly decrease over the next three hours, and then drop by 1 pH unit over the final hour. At hour three the pH measured 11.54, and at hour four the pH measured 10.54. The acid addition was then stopped, and the pH of all three bottles was measured. The pH of Bottle #1 was 10.35, the pH of Bottle #2 was 10.54, and the pH of Bottle #3 was 10.46.

The pH of each test bottle was also measured near the end of the experiment, just before addition of NaOH. The pH was found to decrease slightly from what was measured prior to the peroxide addition, with Bottle #1 (control) showing the greatest change. The measured pH of Bottle #1 was 10.04, Bottle #2 was 10.40, and Bottle #3 was 10.30.

3.2.2 *Color Changes*

During the acid addition the color of the solution changed from yellow to brown. After the peroxide addition began, the 2 test bottles began to turn back to yellow, while the control bottle (not receiving peroxide) remained brown.

The solids isolated from the control bottle at the end of the experiment were beige in color, while the solids isolated from the 2 test bottles were light yellow.

3.3 Sorbate Desorption

As shown in Figure 3-1, a small amount ($\leq$ 4%) of ^{85}Sr was found to desorb when the pH was adjusted to ~11. The solution concentration increased slightly upon the addition of peroxide, but the total percent leached was still below 7%. The small amount of ^{85}Sr that leached during the

peroxide addition, appeared to quickly resorb or precipitate during the hold time, and virtually of the ^{85}Sr was gone from the solution after the addition of NaOH.
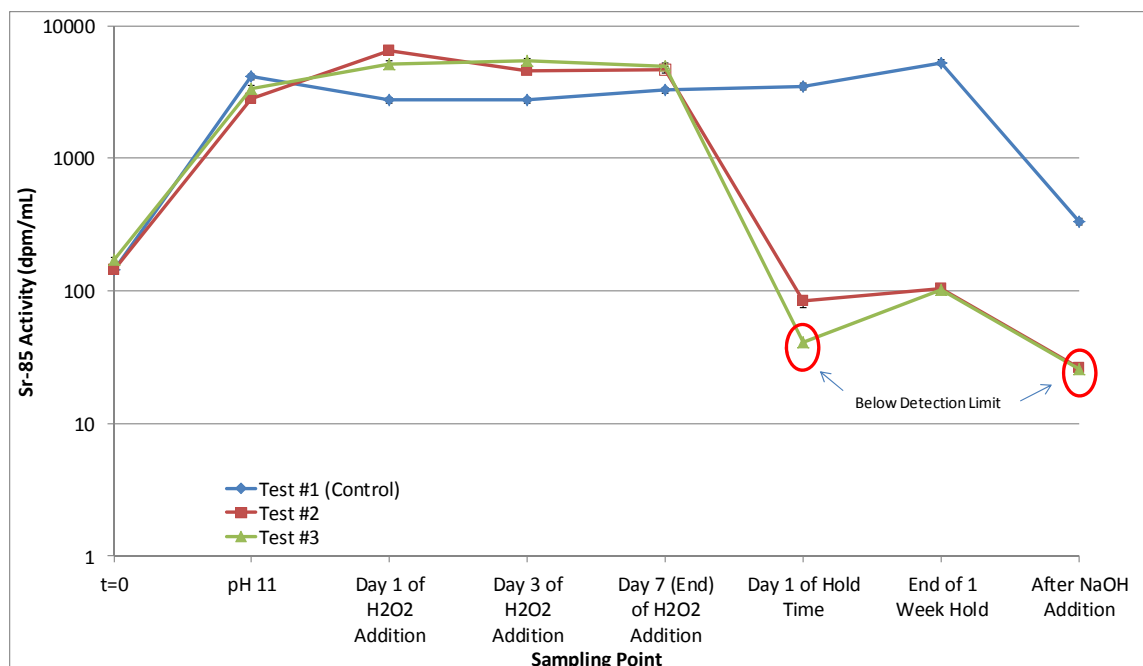

Figure 3-1. ^{85}Sr activity in solution during simulated Tank 48H processing.

Similarly to ^{85}Sr, a small amount (~5%) of the Pu was found to desorb after the acid addition (see Figure 3-2). However, after the peroxide addition began, a significant amount of Pu was found to desorb in the two test bottles, reaching a maximum of ~34% leached 1 day after the peroxide addition began. In the control bottle, which did not receive any peroxide, the Pu was found to precipitate or resorb when the temperature was increased to 50 °C. The Pu in the test bottles remained in solution throughout the peroxide addition, but was gone from solution after 1 day of holding at 50 °C.

As shown in Figure 3-3, a slight increase in the Np solution concentration was also seen after adjusting to a pH of 11. For the test bottles, the Np concentration reached a maximum in solution 1 day after the peroxide addition began. This maximum concentration represents a leaching of ~68-77% of the Np from the MST. After reaching this maximum at the beginning of the peroxide addition, the concentration in solution gradually decreased through the remainder of the peroxide addition, the hold time, and the NaOH addition. The control bottle continued to leach Np into solution during the peroxide addition period, where it was not receiving peroxide, but was at elevated temperature. The control bottle reached a maximum of ~52% leached at the end of the 1 week hold time. The Np then precipitated or resorbed upon the addition of NaOH.
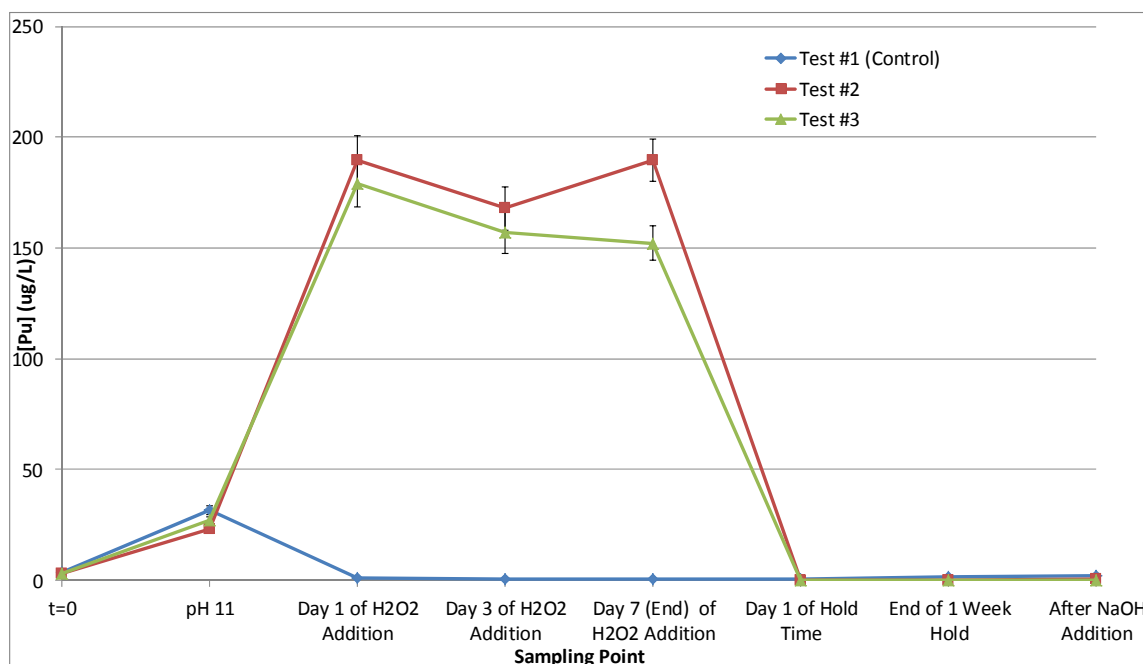
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Figure 3-2. Pu concentration in solution during simulated Tank 48H processing.
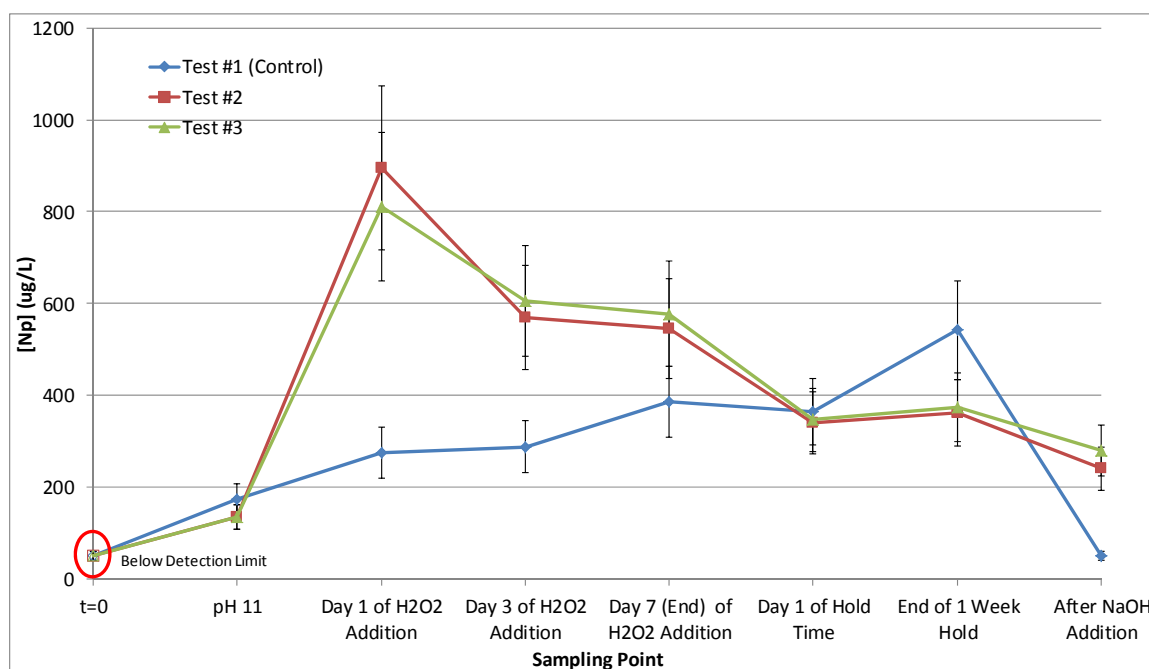

Figure 3-3. Np concentration in solution during simulated Tank 48H processing.

In the control test, U began to desorb from the MST after the acid adjustment, and then continued to desorb throughout the remainder of the experiment (see Figure 3-4). The control bottle reached a maximum desorption of ~58% at the end of the 1 week hold time. A slight decrease in solution concentration was observed after the NaOH addition; however, the majority of U

remained in solution. In the two test bottles, virtually all of the U desorbed at the beginning of the peroxide addition, and remained in solution for the remainder of the experiment, even after NaOH addition, when the other sorbates were found to precipitate or resorb.
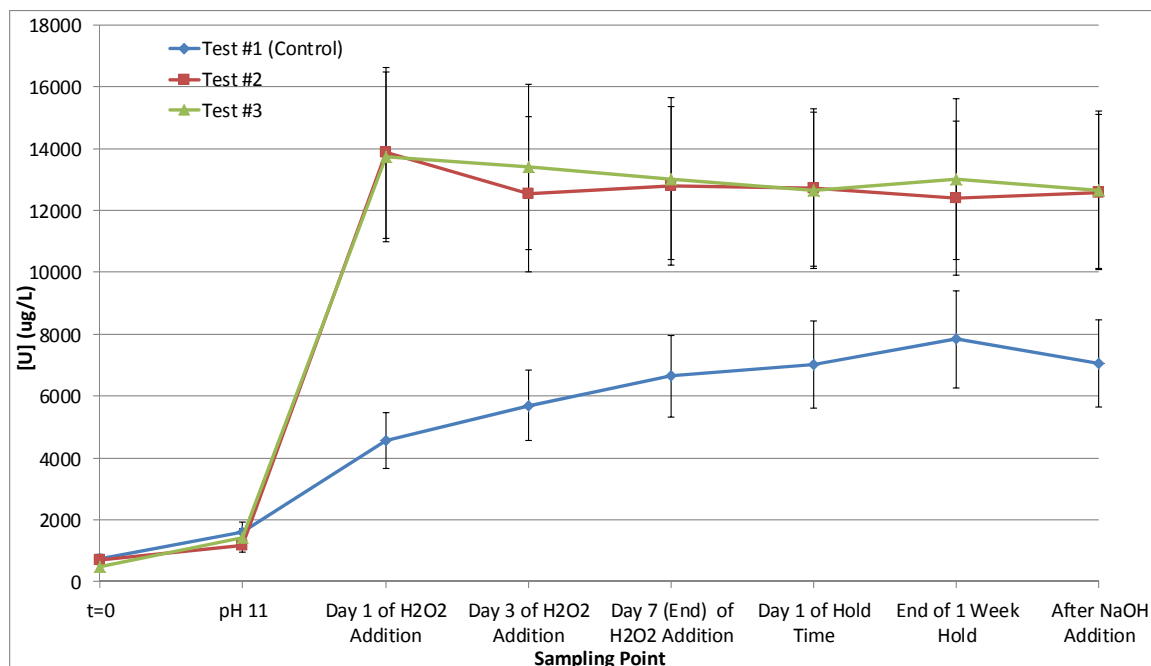

Figure 3-4. U concentration in solution during simulated Tank 48H processing.

In addition to monitoring desorption of sorbates throughout the experiment, the concentration of Ti was measured to monitor the dissolution of MST (see Figure 3-5). No MST was observed to dissolve upon pH adjustment to 11, or upon a temperature increase to 50 °C (control sample). However, significant MST dissolution occurred upon the addition of H_2O_2. The Ti concentration increased throughout the peroxide addition period, reaching a maximum concentration of ~640 ppm, which represents dissolution of approximately 78% of the MST. Assuming the reaction between MST and H_2O_2 is first order with respect to MST, the initial rate of the dissolution of MST can be estimated as 2.3E-04 mol/L·h, with a rate constant of 2.6E-02 h^{-1}. The Ti precipitated from solution after the peroxide addition was complete, as the concentration in solution dropped to ~5 ppm. Some dissolution of MST in the presence of H_2O_2 is expected. During the development of the synthesis for modified MST (mMST), which involves the treatment of MST with H_2O_2 to form a peroxo-titanate, some dissolution of the MST was observed, and it was reported that this dissolution was likely due to excess peroxide present in the synthesis.[12]

The soluble Ti concentration in this experiment was much greater than observed in other CCPO experiments performed using the full simulant make-up, including the TPB. In experiments performed with TPB present, the maximum soluble Ti concentration measured was 62 ppm, which represents dissolution of ~9.4% of the MST available.[9] This test was performed at room temperature with a peroxide addition rate 5 times the nominal rate. These results indicate that the attack of MST by peroxide is significantly suppressed, as expected, by the competing reaction with TPB and other organic components.
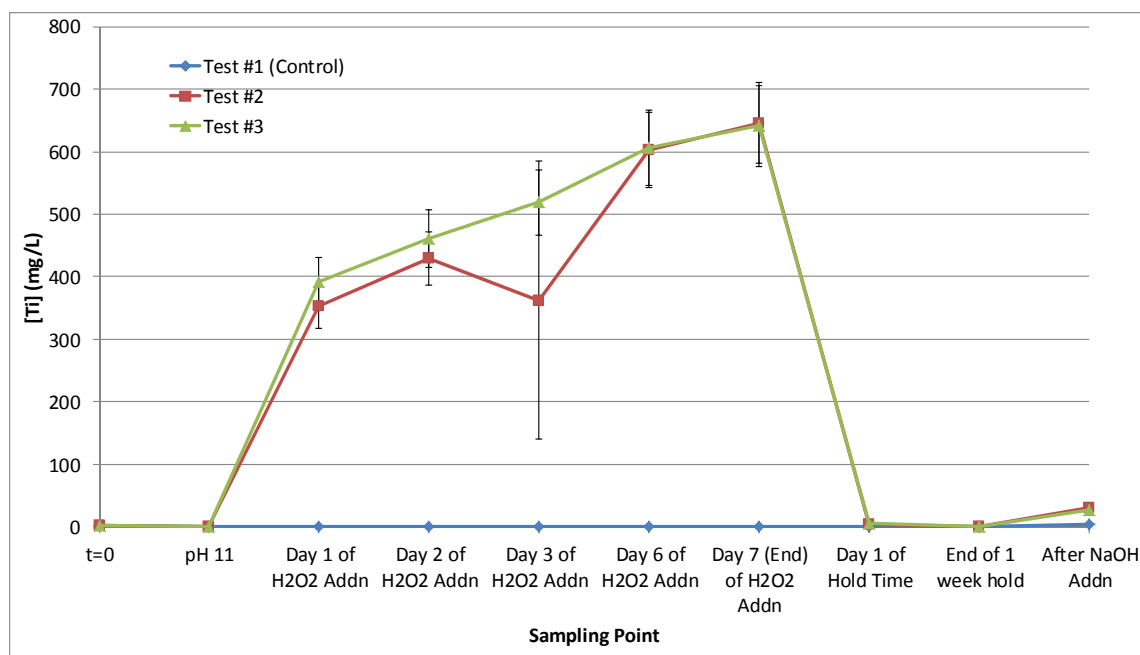
Figure 3-5. Ti concentration in solution during simulated Tank 48H processing.

The dissolution of MST during the hydrogen peroxide addition is consistent with previous findings investigating the synthesis of mMST. One of the alternate methods tested for synthesizing mMST was dissolution of titanium alkoxide in hot (60 °C), strongly alkaline H_2O_2 solution, followed by precipitation of the product.[10] In this synthesis method titanium isopropoxide was added to a 3 M NaOH solution at 60 °C, whereupon a white precipitate immediately formed. H_2O_2 was then slowly added, dissolving the precipitate to form a clear solution. After the H_2O_2 addition was complete, continued stirring of the solution at 60 °C resulted in precipitation of a yellow solid (peroxotitanate). Formation of the peroxotitanate or mMST would be expected to rapidly resorb the Pu and Sr during the 1 week hold time. Since mMST is known to have little affinity for U under these conditions, the observation that U remains in solution is consistent with the formation of mMST upon addition of hydrogen peroxide.

The leaching of Np and U in the control sample is likely due to the formation of carbonate complexes. Np and U exhibit moderate solubilities in the highly alkaline solution with the formation of anionic hydroxyl species such as $UO_2(OH)_4^{2-}$. At lower hydroxide concentrations (i.e., pH 8 to pH ~11.5, uranium exhibits higher solubility due the formation of carbonate complexes such as $UO_2(CO_3)_3^{4-}$.[13] Since the salt solution in contact with the Sr/actinide-loaded MST solids is very high in carbonate (0.455 M), carbonate is likely serving to strip the U and Np from the MST by forming the respective anionic carbonate complexes. Thus, the rate of U and Np leaching in the control sample can be interpreted as the rate of complexation of U and Np by carbonate. After the final pH adjustment to 1 M free hydroxide, the hydroxide species will again be dominant, allowing for resorption of the U and Np onto the MST. Rapid Np sorption was observed. In contrast, only a slight decrease in the U solution concentration was observed upon holding the mixture for 24 hours after the final pH adjustment. The sorption of U onto MST is known to be slow, so a longer hold time would be required to determine if the remaining U would be sorbed by the MST. Carbonate is also known to complex Pu; however, little Pu leaching was observed in the control sample compared to the leaching of Np and U. This observation is

attributed to a stronger interaction between the more highly charged Pu^{4+} compared to the charge of the monovalent neptunyl, NpO_2^+, and divalent uranyl cation, UO_2^{2+}.

Figures 3-6 through 3-8 show the percentage of each sorbate that desorbed during the experiment, along with the percentage of MST that dissolved (by Ti concentration).
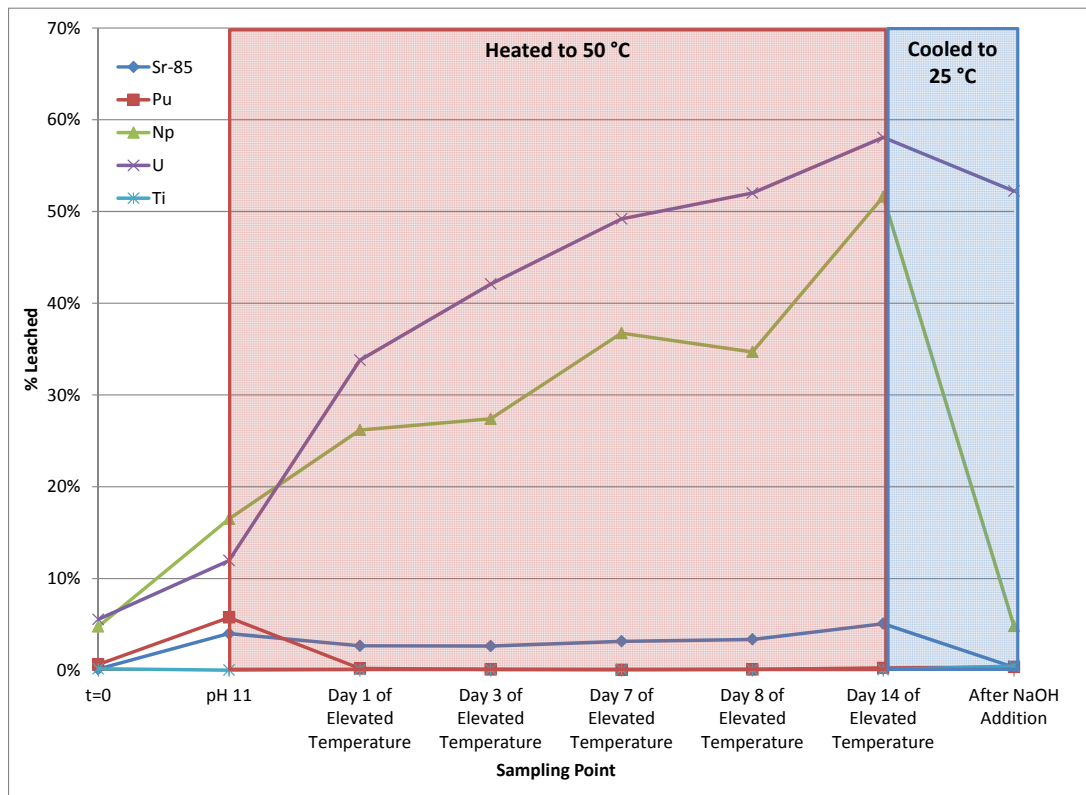

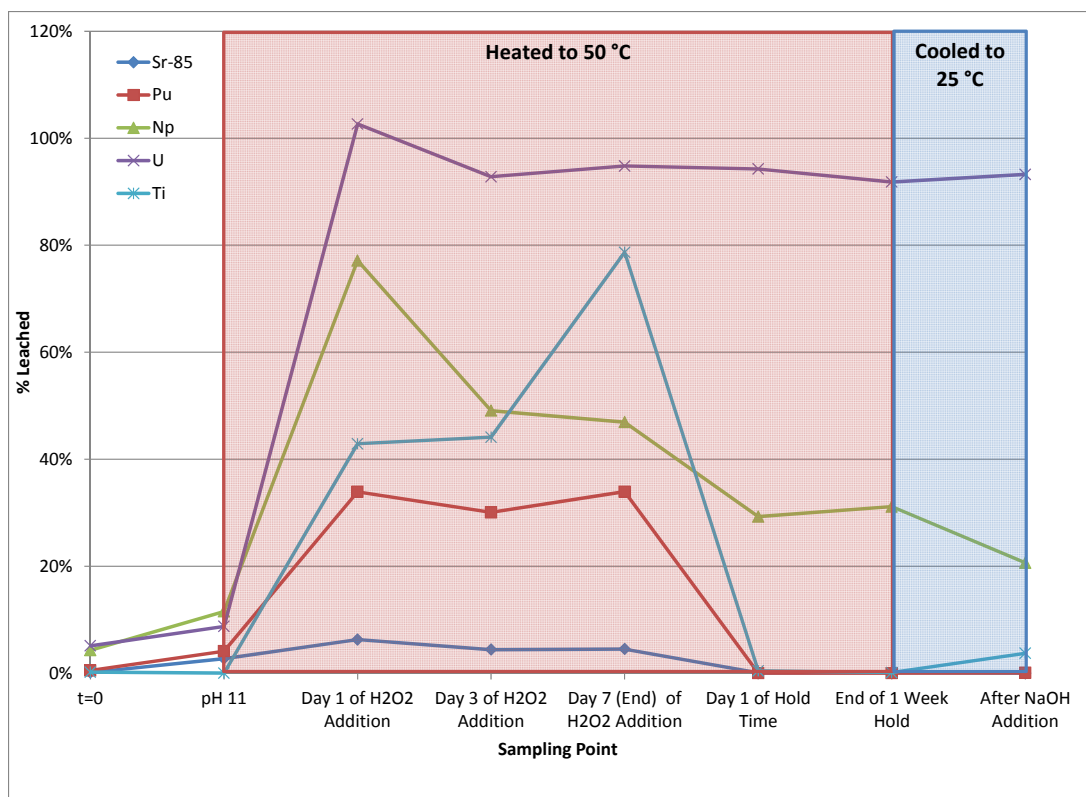**Figure 3-6. Percentage of each sorbate leached during Test #1 (Control).**

Figure 3-7. Percentage of each sorbate leached during Test #2.
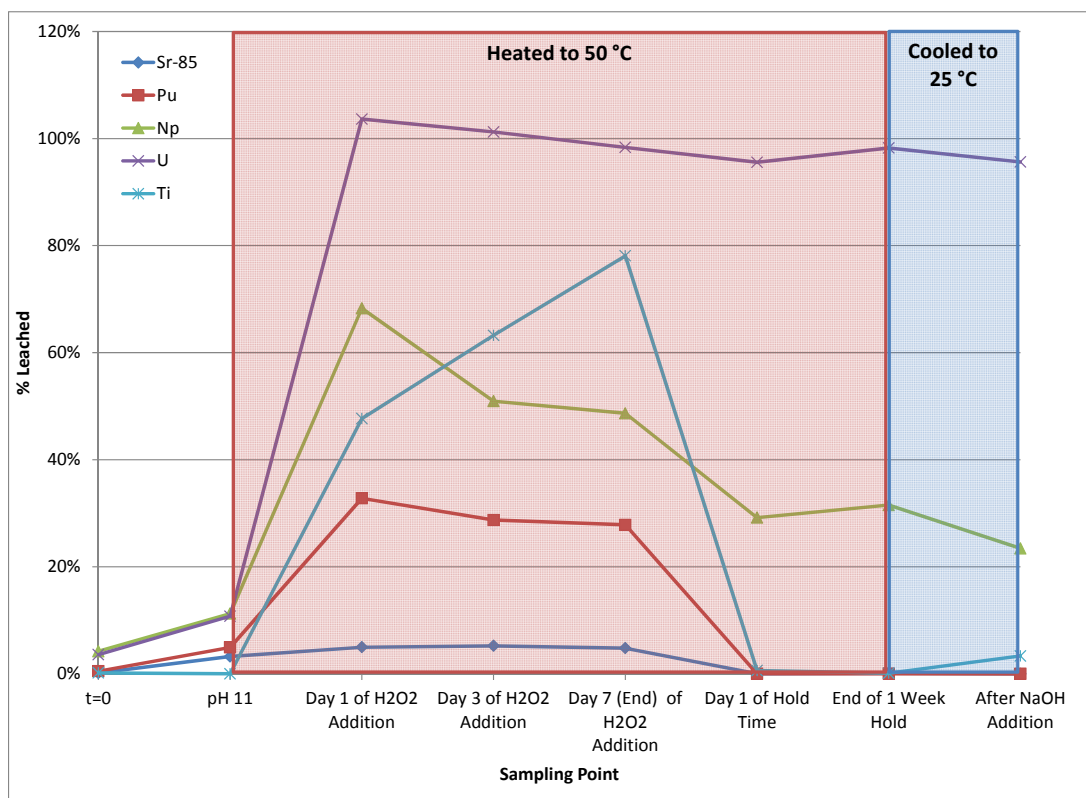

Figure 3-8. Percentage of each sorbate leached during Test #3.

3.4 <u>Analysis of the Solids</u>

The solids recovered at the end of the experiment, after NaOH was added to adjust the free hydroxide concentration to 1 M, were analyzed by several methods. PXRD analysis was performed to potentially identify the form of the precipitated Ti; however, analysis of the solids showed only the presence of sodium salts ($NaNO_3$, $NaNO_2$, $Na_3H(CO_3)_2 \cdot 2H_2O$) and gibbsite ($Al(OH)_3$). Although MST is an amorphous solid, PXRD usually shows evidence of sodium titanium oxide hydroxide ($Na_2Ti_2O_4(OH)_2$), which was not seen in any of the samples from these experiments. A typical MST PXRD is shown in Figure 3-9, and the PXRD patterns from the solids isolated from Tests #1-3 are shown in Figures 3-10 through 3-12.
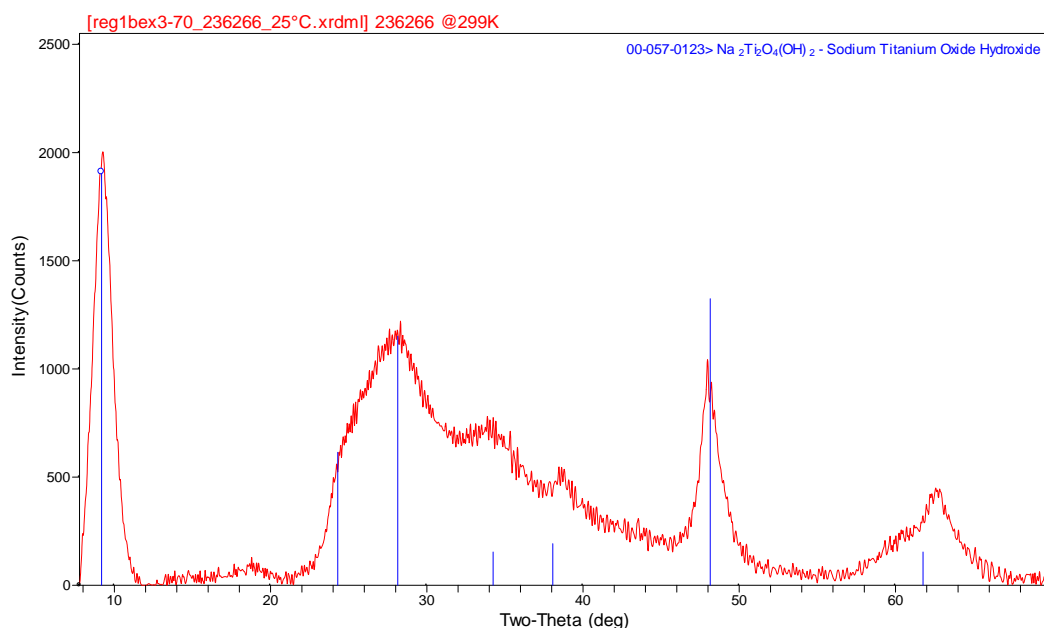

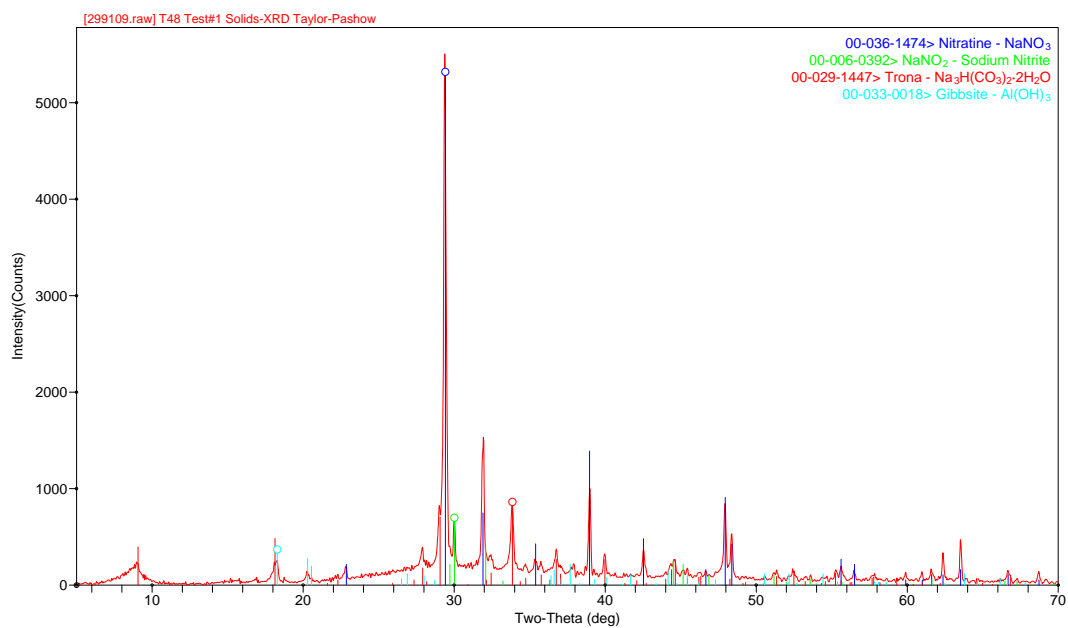**Figure 3-9. PXRD of MST (Optima Lot# 00-QAB-417).**

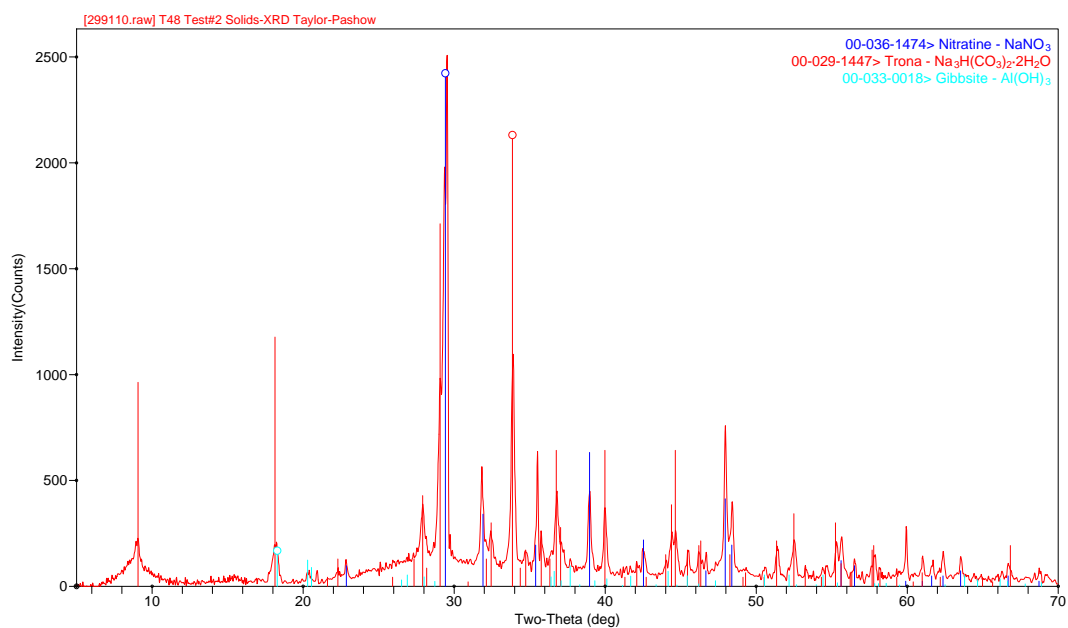**Figure 3-10. PXRD of the solids recovered from Test #1.**

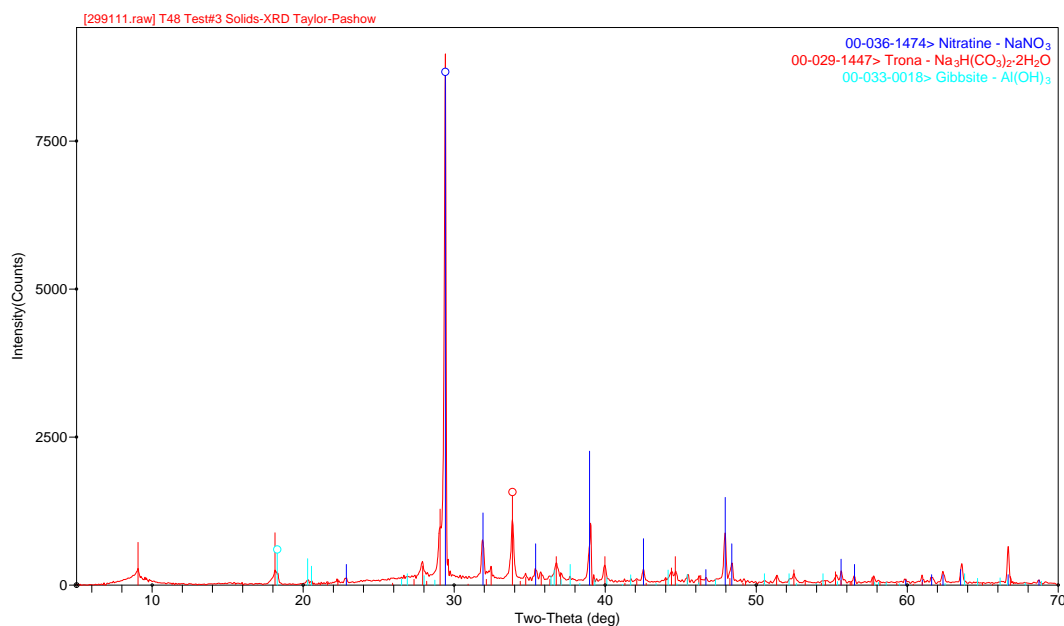**Figure 3-11. PXRD of the solids recovered from Test #2.**

Figure 3-12. PXRD of the solids recovered from Test #3.

Samples of the solids remaining at the end of the experiments were also analyzed using SEM-EDS. EDS analysis did not detect Pu in any of the samples. The Pu concentration in the samples may be below the detection limit of the method. In the EDS analysis, anything below 1 wt % is considered trace concentration and may not be detected. If the Pu present was homogeneous throughout the solid, it would be present at ~0.033 wt %. Some U was detected in the solids isolated from Test #1, but not Tests #2 and 3. This is consistent with the measured solution concentrations, which indicates virtually all of the U leaches from the MST in Tests #2 and 3, and remains in solution; whereas about only half of the U leaches from the MST in the control experiment (Test #1). Representative images and the corresponding EDS spectra are provided in Appendix A. The U concentration in the solids from Test #1 is estimated to be ~0.14 wt %.

In addition to the above analyses, samples of the solids were also dissolved in concentrated sulfuric acid and analyzed for sorbate concentrations and Ti content. The measured sorbate to Ti ratios are provided in Table 3-2. Using the theoretical amount of Ti in MST, these values were converted to the amount of sorbate per gram of MST, to allow for comparison to the initial loading values reported in Table 3-1. The percentages of the initial loadings are also provided in Table 3-2. These measured values are consistent with the solution concentrations measured after the NaOH addition. The analyses of the digested solids show that all of the Sr and Pu originally loaded on the MST is still present with the solids at the conclusion of the experiment, either resorbed or precipitated. For the control sample, this is also true for Np, while in Tests #2 and 3, only about 80% of the Np originally loaded is still present with the solids. This is consistent with the solution analysis, which shows approximately 20% of the Np remaining in the solution. For U, the solids from Test #1 (control) still contain approximately 50% of the U, while the solids in Tests #2 and #3 contain only about 5%, which again is consistent with the solution analysis.

Table 3-2. Measured sorbate concentrations after dissolution of solids in sulfuric acid.

	Test #1	Test #2	Test #3
Sorbate/Ti Ratios			
	Test #1	**Test #2**	**Test #3**
Sr/Ti (dpm/g)	1.52E+08	1.59E+08	1.49E+08
Pu/Ti (µg/g)	7.16E+02	9.08E+02	8.50E+02
Np/Ti (µg/g)	1.31E+03	1.18E+03	1.09E+03
U/Ti (µg/g)	7.77E+03	7.63E+02	8.48E+02
Sorbate/MST Ratios			
	Test #1	**Test #2**	**Test #3**
Sr/MST (dpm/g)	7.30E+07	7.61E+07	7.16E+07
Pu/MST (µg/g)	3.43E+02	4.35E+02	4.08E+02
Np/MST (µg/g)	6.28E+02	5.68E+02	5.22E+02
U/MST (µg/g)	3.72E+03	3.66E+02	4.06E+02
Percentage of Initial Loading			
	Test #1	**Test #2**	**Test #3**
Sr	121%	126%	118%
Pu	107%	133%	128%
Np	103%	83.7%	75.3%
U	47.2%	4.18%	5.25%

4.0 Conclusions

The objective of this study was to examine the fate of fissile material in Tank 48H during the CCPO processing. There are two sources of fissile material – the uranium and plutonium that are sorbed onto the MST and the uranium and plutonium present in the sludge solids. This study only examined the fate of the fissile material on the MST. In addition to the fissile material, the fate of Sr from the MST was also examined. The study found that leaching begins with the pH adjustment. Approximately 5% of the Pu and Sr, 10% of the U, and 10-15% of the Np were found to be in solution after the pH adjustment. The control test provided information on the leaching behavior of the fissile material at elevated temperature in the absence of peroxide. In this test the small amount of Pu that desorbed during the pH adjustment was found to resorb or precipitate upon heating to 50 °C. In contrast, U and Np continued to leach throughout the 2 week period at 50 °C. Np reached a maximum of approximately 52% leached and U reached a maximum of approximately 58% leached. The leached Np was found to precipitate or resorb after the NaOH addition, while the leached U remained in solution. The small amount of Sr that leached during the pH adjustment remained in solution, and then precipitated or resorbed after the NaOH addition. The MST remained intact throughout the experiment for the control sample, indicating that the observed leaching of U and Np in this sample is not due to dissolution of the MST. It is likely that after the pH adjustment to 11, the formation of carbonate complexes with Np and U is resulting in the stripping of these actinides from the MST. The Pu is not stripped due to the stronger interaction of the Pu^{4+} cation compared to the mono and divalent NpO_2^+ and UO_2^{2+} cations.

In the test bottles both U and Pu desorb from the MST when the peroxide addition begins, although to different extents. Virtually all of the U goes into solution at the beginning of the peroxide addition, whereas Pu reaches a maximum of ~34% leached during the peroxide addition. Ti from the MST was also found to come into solution during the peroxide addition. Therefore, Ti is present with the fissile in solution. After the peroxide addition is complete, the Pu and Ti are found to precipitate from solution, while the U remains in solution throughout the remaining

processes, including pH adjustment to 1 M free hydroxide. It is likely that the Ti precipitates as a peroxotitanate material, which can then resorb leached Pu, but has a low affinity for U. The small amount of Sr that leached during the pH adjustment remained in solution throughout the H_2O_2 addition and hold time, but precipitated or resorbed after the NaOH addition. Since Pu was not detected in the SEM-EDS studies, it cannot be conclusively determined in what form the Pu returns to the solids. However, since it is likely a peroxotitante phase is formed under these conditions, the Pu likely resorbed onto this material.

It should also be noted that since the simplified simulant did not contain TPB, all of the peroxide added is available to attack the MST, representing worse case conditions.   However, the experiment may be non-conservative in the fact that the peroxide was added at a faster rate, which leads to a higher rate of auto-decomposition of the peroxide. In addition the absence of the Cu catalyst may also be non-conservative assuming the Cu-peroxide active intermediate is more reactive than the peroxide radical itself.

5.0 Recommendations, Path Forward or Future Work

SRNL recommends the following experiments to further examine the fate of fissile material in CCPO processing of Tank 48H.

- Repeat with full simulant matrix (organic and Cu catalyst present along with simulated radioactive sludge).
- Repeat of one or more of the above tests after selection of final conditions (i.e., pH, temperature) if they differ from conditions tested.

6.0 References

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Appendix A. Supplemental Data

Table A-1. Average Moles of Peroxide versus Ti and Sorbates

Species	Total Moles
H_2O_2	1.182
Ti	0.0034
Sr	1.51 E-06
U	1.17 E-05
Np	9.54 E-07
Pu	4.60 E-07

SEM-EDS Results

In general it is not possible to tell from the following SEM images if the solids are MST or some other amorphous form of Ti precipitate. The MST particles are on the order of ~1 – 10 microns; therefore, the images are of too low magnification to show individual particles.
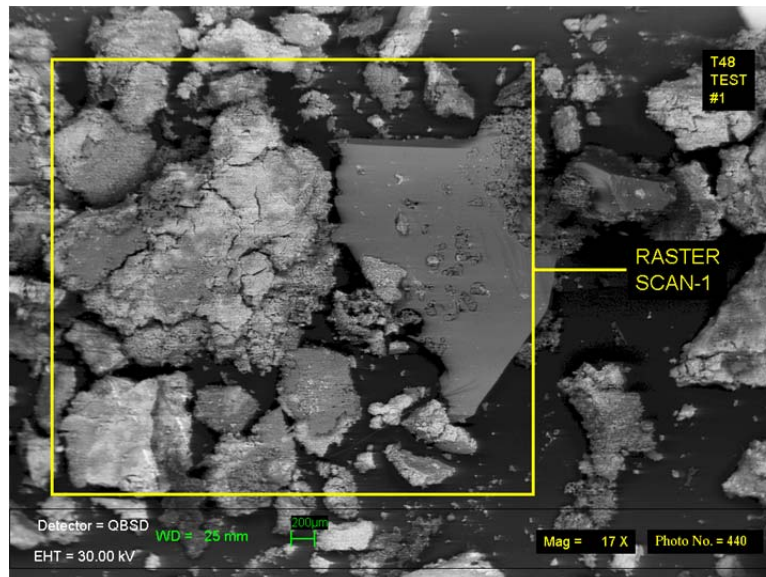
Figure A-1. SEM image of solids isolated from Test #1.
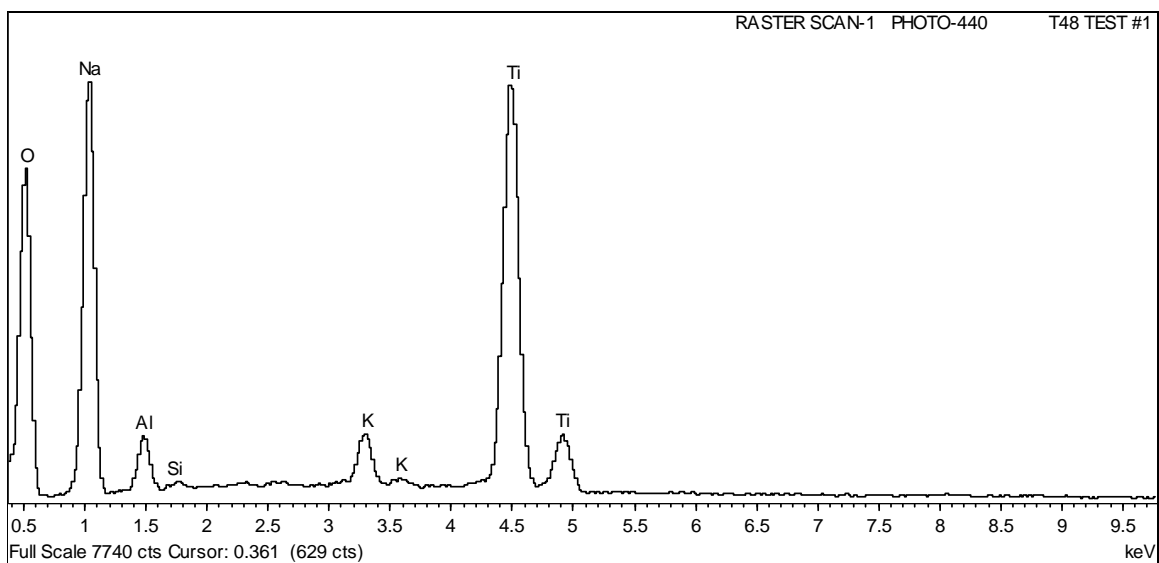
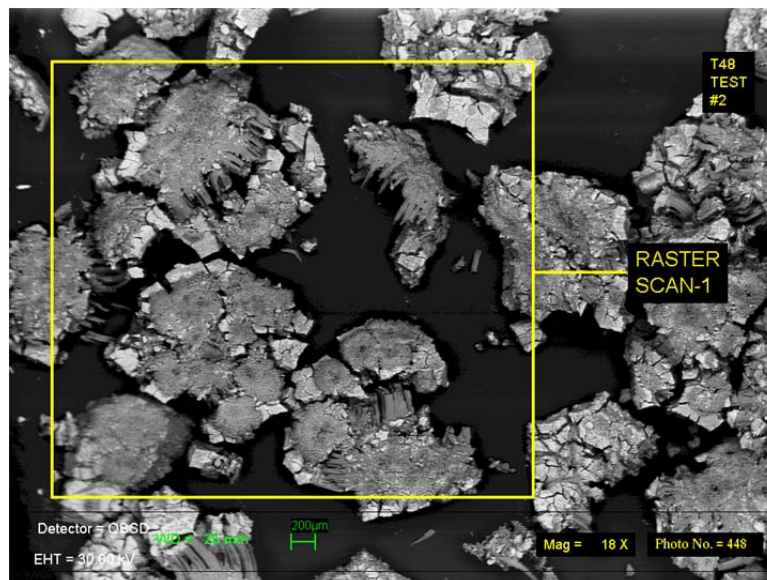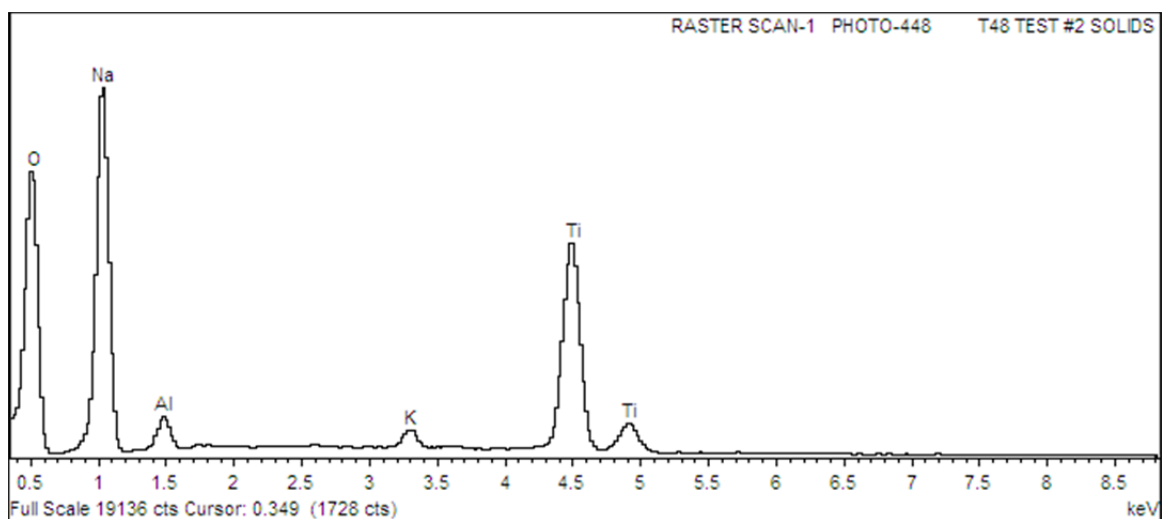**Figure A-2. EDS results from Raster Scan shown in Figure A-1.**
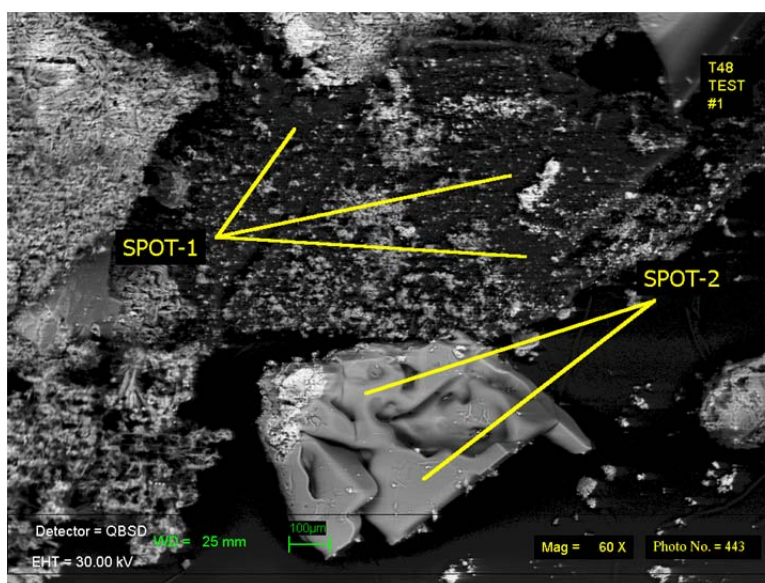
Figure A-3. SEM image of solids isolated from Test #1.
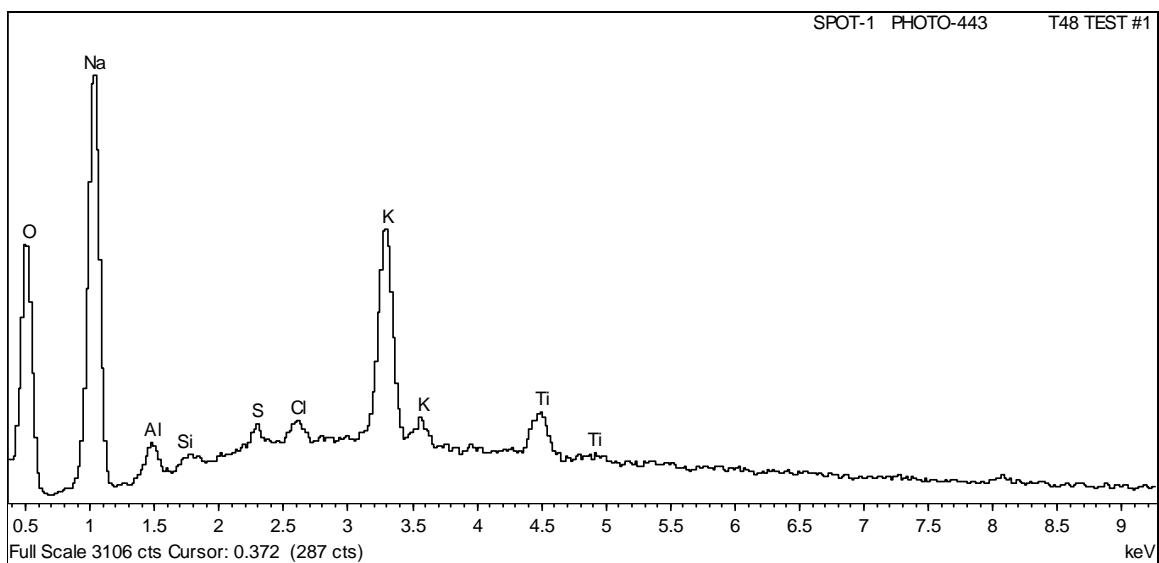
Figure A-4. EDS analysis of Spot-1 shown in Figure A-3.

The EDS spectrum shown in Figure A-5 is indicative of a sodium salt, which could have resulted from residual simulant drying with the solids. This is consistent with the PXRD results which also showed the presence of salts.
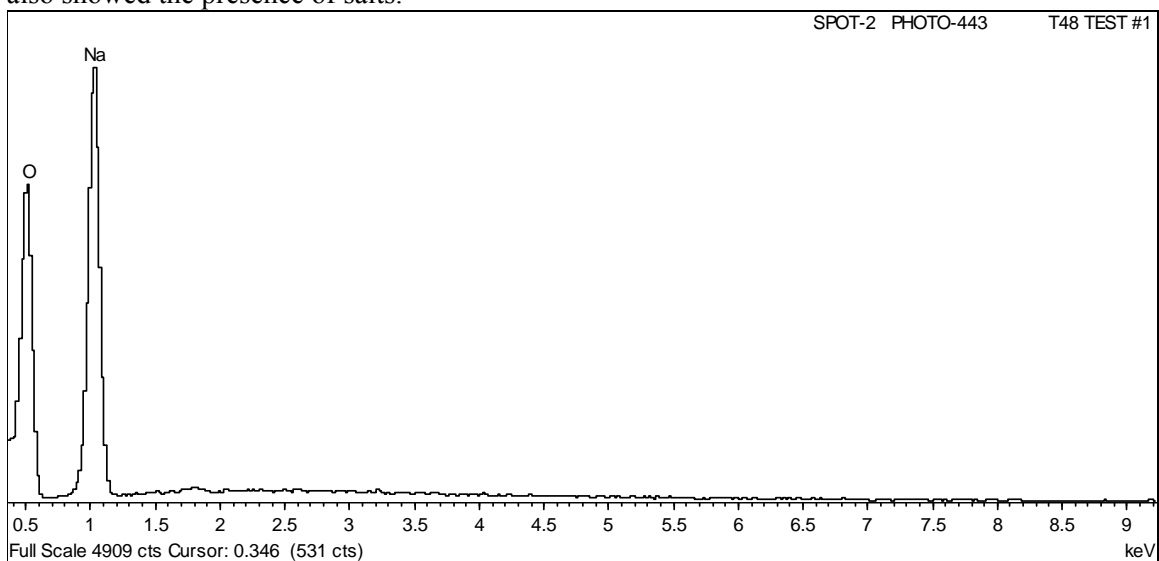
Figure A-5. EDS analysis of Spot-2 shown in Figure A-3.

The bright spots in Figure A-6 suggest U rich areas, as higher atomic number elements appear as brighter spots in a backscatter SEM image. Solution analysis results for Test #1 did not indicate desorption followed by precipitation of U, which would suggest that the U present in the solids is the U originally loaded on the MST.
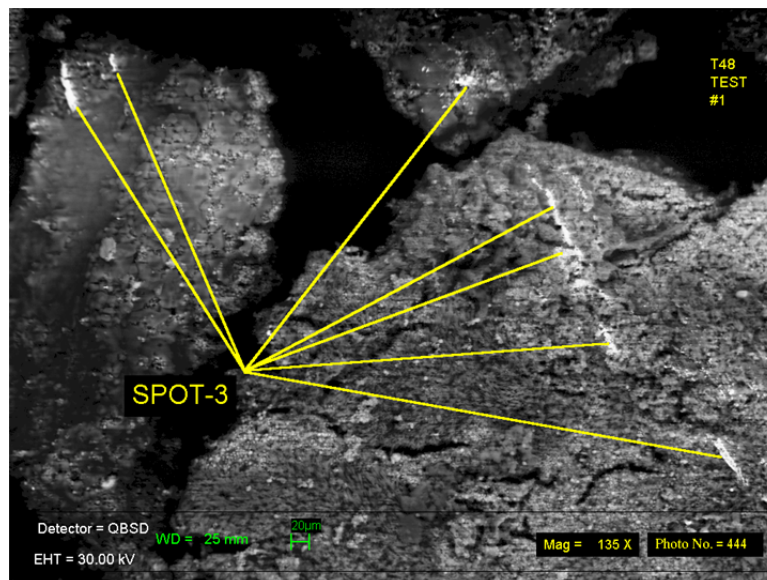
Figure A-6. SEM image of solids isolated from Test #1.
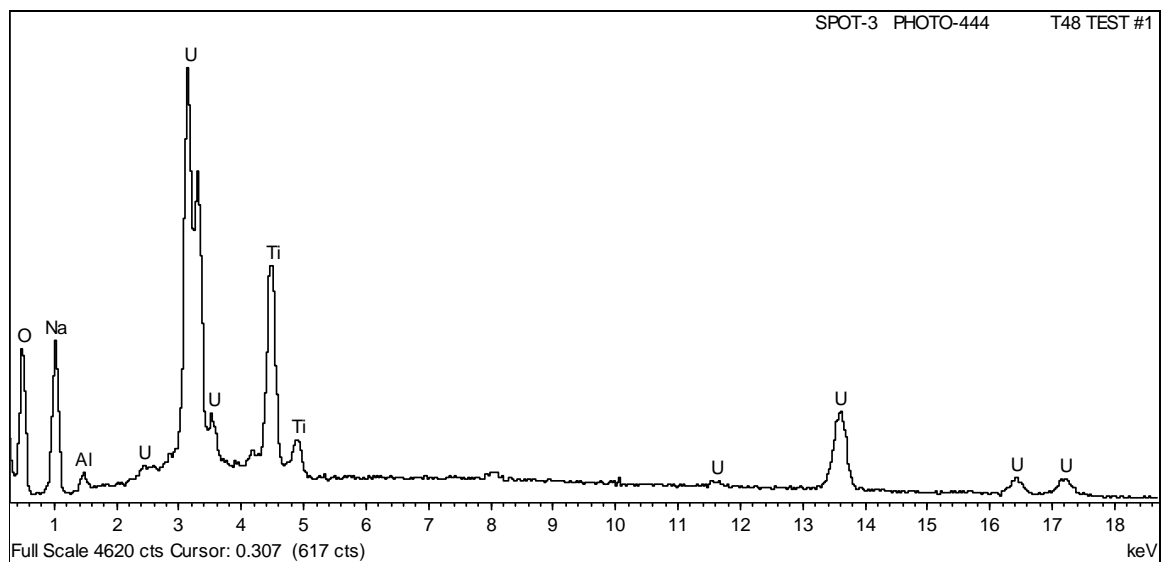
Figure A-7. EDS analysis of Spot-3 shown in Figure A-6.

Figure A-8. SEM image of solids isolated from Test #2.

Figure A-9. EDS results from Raster Scan-1 shown in Figure A-8.
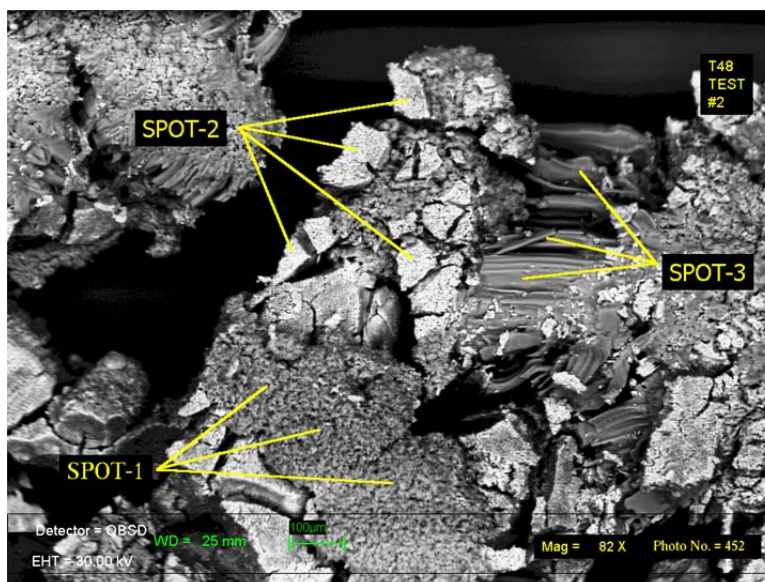
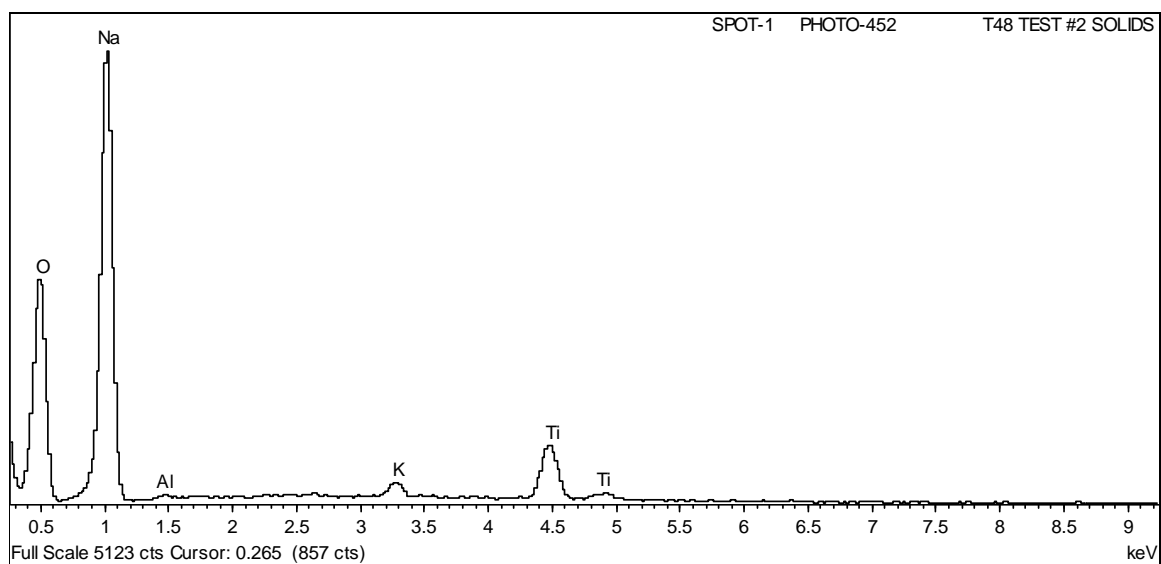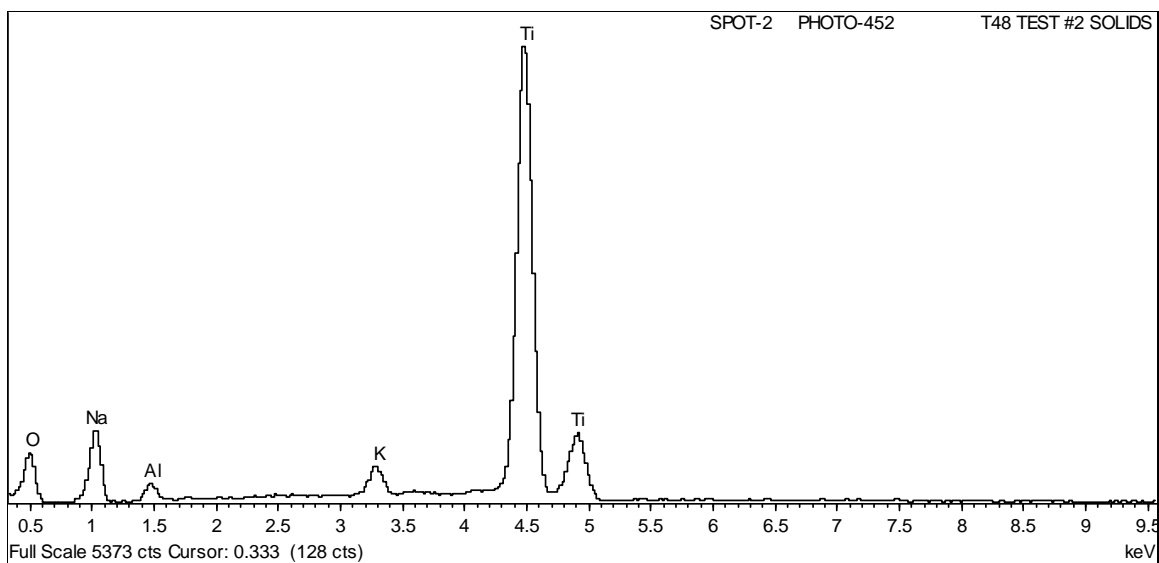**Figure A-10. SEM image of solids isolated from Test #2.**

Figure A-11. EDS analysis of Spot-1 shown in Figure A-10.

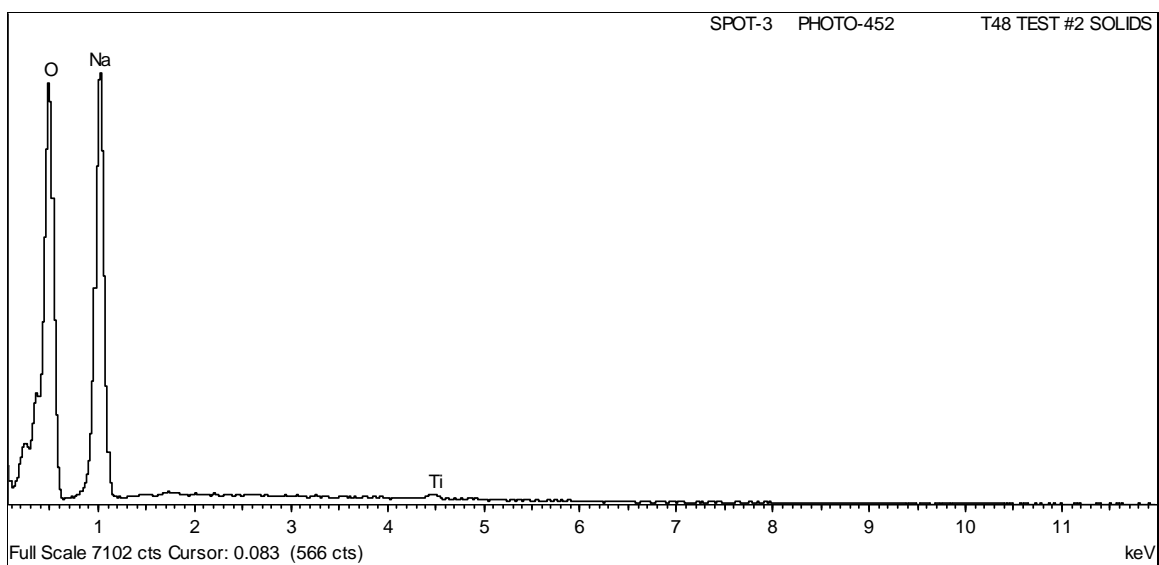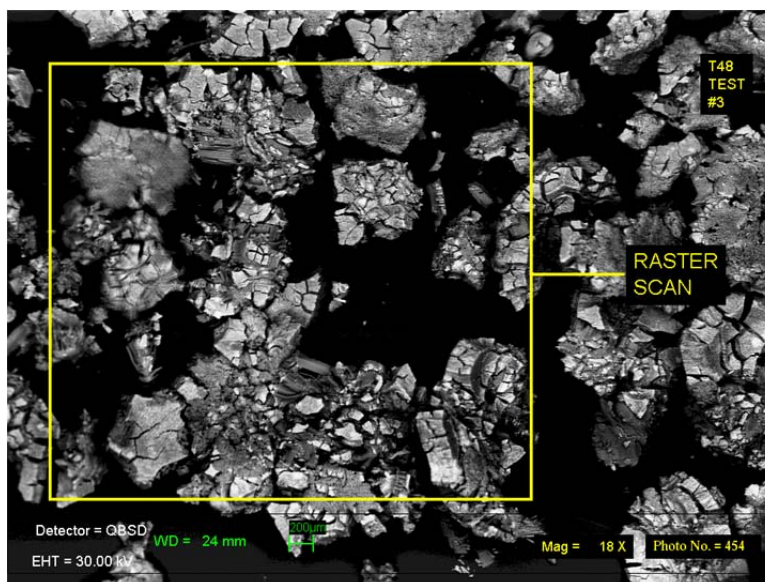**Figure A-12. EDS analysis of Spot-2 shown in Figure A-10.**

Figure A-13. EDS analysis of Spot-3 shown in Figure A-10.
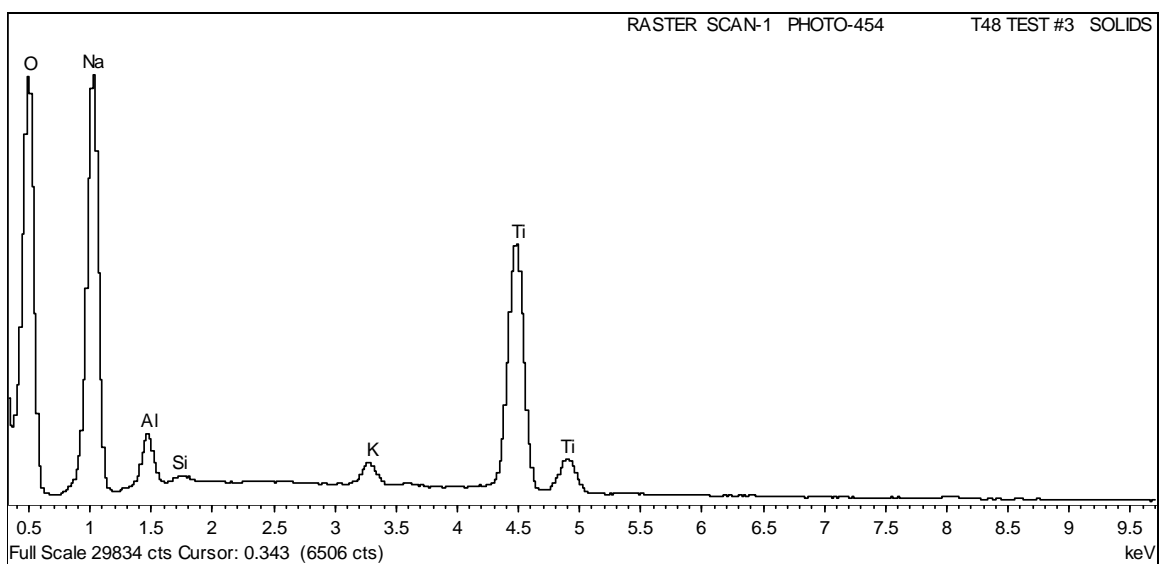
Figure A-14. SEM image of solids isolated from Test #3.

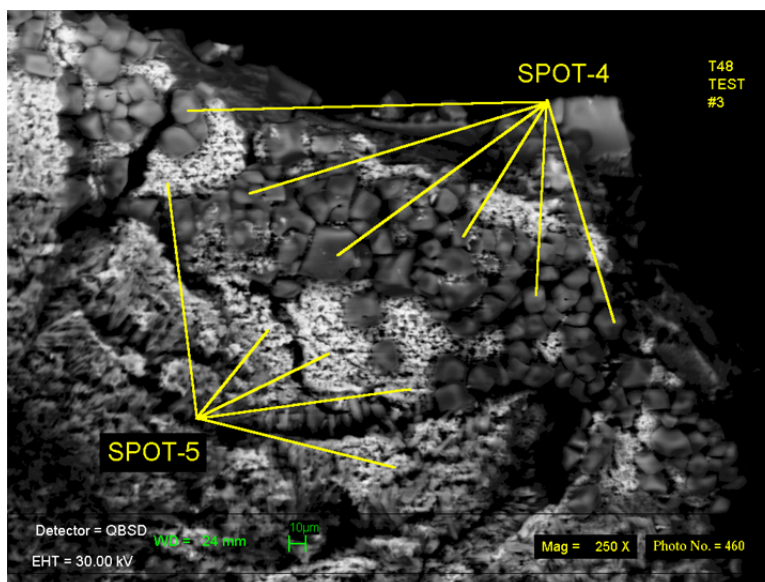**Figure A-15. EDS results from Raster Scan shown in Figure A-14.**

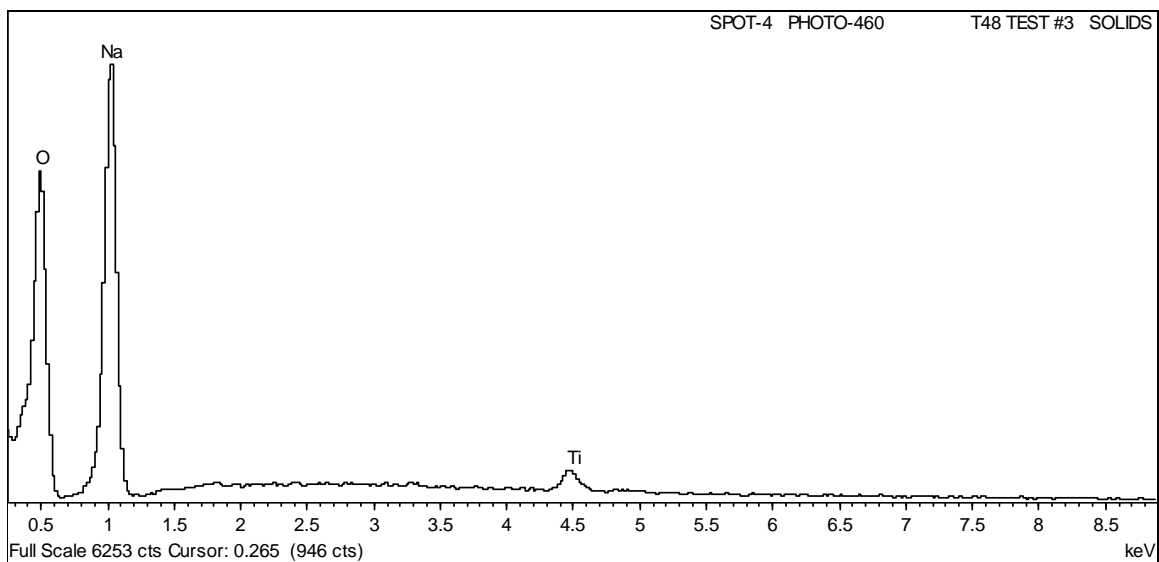**Figure A-16. SEM image of solids isolated from Test #3.**

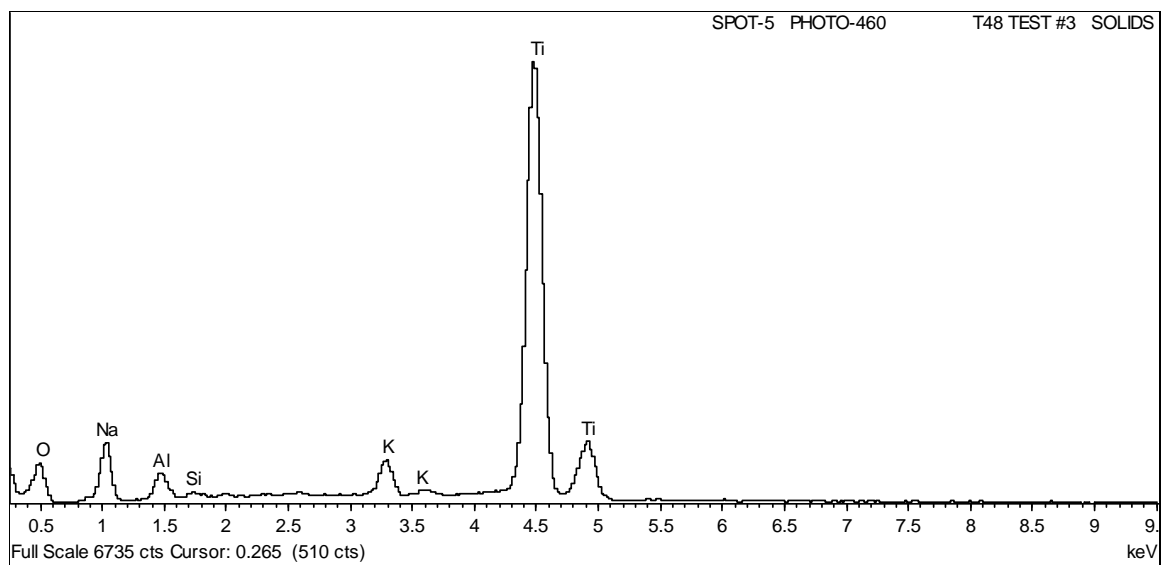**Figure A-17. EDS analysis of Spot-4 shown in Figure A-16.**

Figure A-18. EDS analysis of Spot-5 shown in Figure A-16.

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