RADIOACTIVE DEMONSTRATION OF THE "LATE WASH" PRECIPITATE HYDROLYSIS PROCESS (U)

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The attached report details results of a demonstration of the Precipitate Hydrolysis Process (PHP) using actual radioactive precipitate. This report documents work fulfilling the SRTC milestone on this subject. The radioactive tetraphenylborate (TPB) precipitate was from Tank 48 and contained large amounts of Cs-137. The PHP demonstrated by this work is that which would be performed after late wash. Hydroxylamine nitrate (HAN) was not included in this PHP. The PHP demonstrated by this work would be performed in the Salt Processing Cell in the DWPF after late wash. It was decided not to demonstrate the PHP requiring HAN for the following reasons: 1) Tank 48 material was too high in both nitrite and hydroxide to be processed in DWPF with the HAN PHP, 2) the Late Wash Flowsheet has been shown to be superior to the flowsheet requiring HAN, 3) there was a very limited amount of radioactive TPB precipitate available, and 4) there are possibilities of high radiation exposures to personnel and other difficulties can be expected in obtaining more TPB precipitate from Tank 48.

The precipitate in Tank 48 resulted from a successful demonstration in April, 1983, of the In-Tank Precipitation Process. A portion of this precipitate and its associated supernate were transferred to the Shielded Cells of SRTC where the PHP demonstration was performed. The original slurry from Tank 48 had 2X too much nitrite even for the PHP with HAN. The precipitate was washed to the nitrite concentration expected from the late wash flowsheet (0.01M). This also diluted the hydroxides. The radioactive precipitate was then hydrolyzed using Cu(II) and formic acid without the addition of HAN. The radioactive demonstration was successful in that no differences were observed between
hydrolyzing radioactive precipitate and nonradioactive simulated precipitate. Cesium-137 in the precipitate was solubilized and benzene was distilled from the hydrolysis mixture. Mass balances based on Cs-137 as well as K and B were good. The decontamination of the benzene condensate was such that it appears that the decontamination of the organic condensate in the DWPF will be successful. Although we are unable at this time to analyze the radioactive solutions for residual organics, the hydrolysis reaction went smoothly and the appearances of the products were similar to those in nonradioactive tests where the organic was removed. Future radioactive tests will concentrate on measuring these residual organics as well as the fate of the minor fission products (such as Sr -90) and actinides (such as U and Pu) in the hydrolysis reaction.

Questions regarding the attached report should be directed to N. E. Bibler, 773-A (Ext. 52313) or D. M. Ferrara, 773-62A (Ext. 55344).

E. W. Holtzscheiter, Manager, SRTC-DWPT Section

Authorized Derivative Classifier

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June 30, 1992

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RADIOACTIVE DEMONSTRATION OF THE "LATE WASHED"
PRECIPITATE HYDROLYSIS PROCESS

ABSTRACT

This report presents results of the radioactive demonstration of the DWPF Precipitate Hydrolysis Process as it would occur in the "late wash" flowsheet in the absence of hydroxylamine nitrate. Radioactive precipitate containing Cs-137 from the April, 1983, in-tank precipitation demonstration in Tank 48 was used for these tests. Two tests were performed remotely in the shielded cells of SRTC. A sample of the precipitate slurry from Tank 48 was transferred to

Authorized Derivative Classifier

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SRTC and adjusted to have a composition expected from the currently proposed late wash process. These adjustments included reprecipitating the Cs-137 which had been released by radiation while the slurry was stored in Tank 48 and washing the precipitate to achieve a nitrite concentration of 0.01 M. Results of the two hydrolysis tests indicated that the radioactive tetraphenylborate precipitate can be successfully hydrolyzed to solubilize all the Cs-137 as well as the K and B in the precipitate. Further, there were no significant observable differences between the radioactive hydrolysis reaction and the reaction using simulated nonradioactive precipitates. The fresh Cs-137 precipitate floated and foamed when stirred. This was observed with simulated precipitate. The old Cs-137 precipitate settled to the bottom of the slurry and did not foam as with simulated irradiated precipitate. During the radioactive hydrolysis reaction all color changes were identical to those observed in the nonradioactive reaction. Benzene that was nearly free of Cs-137 was distilled from the radioactive reaction mixture suggesting that benzene decontamination in the DWPF will be successful. Mercury was also distilled from radioactive reaction mixture. Finally, in addition to Cs-137, the radioactive precipitate contained fission products Rb-85, Rb-87, and Sr-90, and the actinides U and Pu.

INTRODUCTION

Currently, there are 130 million liters of caustic radioactive waste being stored in the Tank Farm at the Savannah River Site (SRS). This waste consists of caustic sludges and supernates. The supernates contain most of the Cs-137 (which is soluble in the caustic) along with lower concentrations of other radionuclides such as strontium-90 and plutonium-239. The sludges contain all those radionuclides that are insoluble in caustic. The radionuclides in the sludges and supernates are to be immobilized by vitrification into a borosilicate glass in the Defense Waste Processing Facility (DWPF). Before feeding this waste to the DWPF, it must be treated to make it compatible with the immobilization technique. Radionuclides have to be removed from the supernates. This is to be done by precipitating the soluble fission product Cs-137 as cesium tetraphenylborate (CsTPB), and adsorbing the less soluble radionuclides, such as strontium-90 and plutonium, on sodium titanate. Potassium is also precipitated by this process. This precipitation process was demonstrated successfully in the Tank Farm in April, 1983, in Tank 48 using the in-tank precipitation (ITP) process. Once the
radionuclides are removed from the supernate, the decontaminated liquid will be disposed of as saltstone.1

Before mixing the resulting CsTPB slurry with the sludge for final vitrification, the precipitate must be treated to destroy the organic portion of the tetraphenylborate (TPB) precipitate. This is necessary to ensure that most of the organic material is not fed to melter. To destroy the TPB, the Precipitate Hydrolysis Process (PHP) was developed using formic acid for the hydrolysis and hydroxylamine nitrate (HAN) to mitigate the effects of nitrite in the slurry. Later it was found that HAN led to ammonium nitrate formation. To mitigate ammonium nitrate production the late wash flowsheet3 was developed and which eliminated the need for HAN in the PHP.4

This PHP is based on cleavage of the four boron-phenyl bonds in the TPB anion to form benzene. Although the first three of these bonds can be broken by the formic acid at elevated temperatures (~100°C), cleavage of the final bond requires a catalyst. For this purpose, copper in the form of copper formate tetrahydrate is added to reaction vessel. The initial part of the hydrolysis reaction is run at 90°C. At this temperature, most of the benzene is distilled from the reaction mixture. The mixture is then refluxed at approximately 100°C to complete the hydrolysis and distill off the residual benzene. Any mercury which may be present is also distilled at this time.

The PHP has been optimized and demonstrated with nonradioactive precipitate slurries especially prepared to simulate the actual radioactive slurries.5 The goal of the PHP tests described in this report was to demonstrate the current PHP (in the absence of HAN) using the radioactive TPB slurries generated by the ITP demonstration in Tank 48. Approximately 1.4 liters of radioactive precipitate slurry was obtained from Tank 48 and transported to Savannah River Technology Center. A portion of this slurry was used in this study of the radioactive PHP.

The precipitate sample obtained from Tank 48 was approximately nine years old. Consequently, radiolysis had destroyed some of the TPB and released Cs-137 to the supernate. Thus, the sample was reprecipitated and washed before the PHP experiments were made. The final washed precipitate and supernate were sampled and analyzed. Additions were then made so that the final slurry had the same concentrations of nitrate, nitrite, hydroxide, and solids as
expected from the late wash process. Two hydrolysis tests were then performed using the radioactive precipitate slurry.

EXPERIMENTAL

Approximately 1.4 L of highly radioactive precipitate slurry from the ITP process in Tank 48 was delivered to Savannah River Technology Center (SRTC) Shielded Cells Operations (SCO) by Waste Management Operations personnel. The ITP demonstration was completed in April 1983. To collect the 1.4 L sample from the tank, several open 100 mL steel bottles had to be individually lowered to the bottom of Tank 48. At this time there were approximately 20,000 gallons in the tank. After each bottle was filled, it was pulled out of the tank, and capped remotely. Nineteen bottles were necessary to obtain sufficient sample for the PHP demonstration at SRTC. The 100 mL bottles were delivered to SCO in two batches, one batch on September 24, 1990, and the other on November 3, 1990. These were then combined on November 14, 1990, to form the 1.4 L sample shown in Figure 1. This picture is taken through the window of the shielded cell. At this time, the slurry was approximately eight years old and had thus been exposed to considerable radiolysis in Tank 48. In Figure 1, the TPB precipitate has settled and the supernate is dark brown due to water soluble radiolytic products. Based on the concentration of Cs-137 present (approximately 4 Ci/gal) the slurry had received a dose of approximately $1.4 \times 10^8$ rad by April 1992 when the PHP tests started.

As an initial characterization step, the slurry was mixed and a small sample centrifuged. Figure 2 shows the resulting material in a centrifuge cone being held by a manipulator. After centrifugation, three phases were present. These were a heavy precipitate phase at the bottom of the centrifuge vial, a dark brown supernate phase, and a lighter precipitate phase on top of the supernate. Note that there are apparently solids of many densities present. The original 1.4 L sample was then divided. One half was washed as in the late wash process and the other half retained for future tests. Inhibited water similar to that used in the Tank Farm (0.015 M NaOH) was used in the wash process.
Figure 1. Radioactive TPB Precipitate from Tank 48. The Precipitate is ~9 Years Old and Has Received a Dose of 1.4E08 Rads.
Figure 2. Centrifuged Radioactive KTPB from Tank 48.
To perform the PHP tests, the amount of formic acid to add for hydrolysis had to be determined. Sufficient formic acid is needed to neutralize the caustic in the slurry to a pH of 5.5 and to produce a PHA with 0.25 M excess formic acid above that required to completely hydrolyze the tetraphenylboron to benzene.\(^4\)

To calculate the amount of formic acid necessary for the hydrolysis reaction, the concentration of TPB in the precipitate slurry must be known. This concentration was determined by the DWPF method specifically developed for this purpose.\(^7\) The elemental composition of the solids was determined using a peroxide fusion dissolution method and analyzing the resulting solution by ICP-ES and radioactive counting. This is the DWPF method developed for radioactive sludges and glasses.\(^8\)

After the precipitate was washed and sufficiently characterized, the two precipitate hydrolysis tests were performed. For these first two tests, 0.7 L of the original sample from Tank 48 was used. These tests were performed remotely by SCO personnel. The apparatus used is shown in Figure 3. The reaction takes place in the reaction vessel on a hot plate. Mounted on top of the reaction vessel is the decanter which allows the organic condensate to be collected and the aqueous condensate to be returned to the reaction vessel. Above the decanter is a condenser which was kept at 15\(^\circ\)C. Protruding into the reaction vessel is a tube through which the precipitate slurry was fed, a pH electrode, and a thermocouple for measuring the temperature. The procedure used is in Table 1. This procedure is identical to that used in larger scale studies with simulated precipitate slurries.\(^4,5\) The concentration of copper used as a catalyst was 800 ppm. For the first test, 200 mL of slurry and 14 mL of 90 percent formic acid were used. For the second, the values were 183 mL and 12.6 mL respectively.

After each test, the aqueous product, the aqueous and organic condensates, and the solutions in the decanter were sampled for analysis. In the second test, the composition of the evolved gas was determined using Ar to sweep the gases through a gas chromatograph. In both tests, because of the high radiation levels of the Cs-137, the Precipitate Hydrolysis Aqueous (PHA) product had to be diluted by a factor of 700. A small aliquot of this dilution was then taken out of the shielded cells. This dilution was necessary to reduce radiation exposure to personnel. The condensates and decanter solutions could be removed without dilution.
Figure 3. Precipitate Hydrolysis Reactor Prior to Being Put into the Shielded Cells.

Condenser
Thermocouple
Decanter
pH Probe
Condensate Collector
Reaction Vessel

NO FILE NUMBER
Table 1. Procedures for the Radioactive Precipitate
Hydrolysis Tests in the Absence of HAN

- Add formic acid and copper formate to the reaction vessel.
- Heat the reaction vessel to 90°C.
- Add precipitate slurry to the formic acid and copper formate.
- Keep the reaction vessel at 88 to 92°C for 5 hours.
- Bring the reaction mixture to a boil.
- Boil the mixture for 5 hours.

aTaken from reference 4.

RESULTS AND DISCUSSION

Results collected during the two tests included analyses of the precipitate feed, observations made during the hydrolysis tests, and analyses of the reaction products. The results suggest that the currently proposed PHP will be successful in hydrolyzing radioactive TPB precipitate from ITP. Also, it appears that radioactive slurry and nonradioactive simulated slurry react in essentially the same manner. Prior to the tests, however, it was necessary to reprecipitate the Cs-137 due to radiolysis destroying the precipitate during storage in Tank 48.

Reprecipitation of the Cs-137

Since the slurry was approximately nine years old, sufficient radiolysis had occurred to destroy some of the TPB and release Cs-137 and potassium to the supernate. Consequently, fresh NaTPB was added to the supernate to reprecipitate this Cs-137 and potassium. The precipitate was then washed to dilute the NO$_2^-$ and Na$^+$ to the levels expected in the late wash flowsheet.\(^3\) Concentrations in the initial and final solutions in this wash process are shown in Table 2. The large Na$^+$ concentration is a result of adding NaOH while the slurry was in Tank 48 to inhibit corrosion of the tank. An analysis of the original supernate gave a hydroxide concentration of approximately 3M. After washing, the Na$^+$, B, NO$_2^-$, NO$_3^-$, and Cs-137 concentrations had dropped by factors in the range of 20 to 30 while K$^+$ had dropped by a factor of 70. The drops in Na$^+$, B, NO$_2^-$,
and NO3- are probably due mostly to washing and dilution of the supernate while those for K+ and Cs-137 also involves reprecipitation. It appears that the final concentration of Cs-137 is slightly higher than the 1000 nCi/g limit for saltstone feed.

Table 2. Concentrations of Soluble Ionic Species in the Radioactive Tank 48 Precipitate Slurry

<table>
<thead>
<tr>
<th></th>
<th>Moles/Liter</th>
<th>nCi/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NO2-</td>
<td>NO3-</td>
</tr>
<tr>
<td>9 Year Old Slurry</td>
<td>0.38</td>
<td>0.042</td>
</tr>
<tr>
<td>Supernatea</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Washed Slurryd</td>
<td>0.011e</td>
<td>0.002</td>
</tr>
</tbody>
</table>

aThis is the supernate of the slurry shown in Figure 1 and Figure 2.
bSoluble boron resulting from radiolysis products of TPB.
cThe limit for saltstone feed is 10³ nCi/g.9
d0.39 L of 9.35 weight percent solids.
eThe goal for the late washing flow sheet will be < 0.01 M.

Composition of the TPB Precipitate

The composition of the TPB precipitate is given in Table 3. This composition is given in units of weight percent of solids resulting from drying at 110°C an aliquot of the slurry. The slurry itself was 9.35 wt % solids. Note that on a molar basis the potassium, boron, and TPB concentrations are nominally the same. This was expected since on a mass basis, the majority of the precipitate is KTPB which contains one mole of K per mole of B and TPB.

Titanium made up 5.53 wt percent of the solids. Sodium titanate (NaTi2O4) was added to Tank 48 to remove residual traces of strontium-90 and plutonium from the supernate. Assuming the titanium was present as NaTi2O4, the titanium compound would make up 11.5 wt percent of the solids. This concentration is about twice concentration in the expected feed to the DWPF salt cell.10 The difference may be due to the sampling technique in Tank 48. The
titanium solids may have settled before the lighter KTPB precipitate since originally the precipitate floats. The samples taken from the bottom of the tank may not have been representative of the total precipitate in Tank 48.

Table 3. Composition of KTPB Precipitate in the Feed Slurry

<table>
<thead>
<tr>
<th></th>
<th>Wt Percent</th>
<th>mCi/g</th>
<th>Moles/100 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>1.41 ± 0.08&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-------</td>
<td>0.13</td>
</tr>
<tr>
<td>K</td>
<td>6.28 ± 0.54&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-------</td>
<td>0.16</td>
</tr>
<tr>
<td>TPB&lt;sup&gt;-&lt;/sup&gt;</td>
<td>50.3 ± 0.96&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-------</td>
<td>0.16</td>
</tr>
<tr>
<td>Ti</td>
<td>5.53 ± 0.31&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>Cs-137</td>
<td>-------</td>
<td>25.3 ± 1.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-------</td>
</tr>
</tbody>
</table>

<sup>a</sup>Average of duplicate analyses<br>
<sup>b</sup>Average of triplicate analyses

The Cs-137 concentration reported in Table 3 was used in mass balance calculations presented later in the report. It was also used to estimate the Cs-137 concentration in the original 0.7 L taken from the bottle shown in Figure 1. After washing, a total of 0.39 L of washed slurry was obtained from the original 0.7 L. The percent solids in the final product was 9.35 % (average of duplicate results). Thus, the total activity was 0.97 Ci. This gives an original concentration of 1.4 Ci/L or 5.2 Ci/gallon. This concentration is nominally 5 times smaller than the 24 Ci/gallon expected in the initial slurries when ITP starts.

Other analyses indicated that the precipitate from Tank 48 also contained minor amounts of the fission products strontium-90, rubidium-85, and rubidium-87 along the actinides plutonium, and uranium. These results will be discussed in a later report.

Observations during the Two PHP Tests

During the PHP tests, the colors of the products were noted, and foaming of the precipitate feed was observed. These observations were similar to those seen with larger scale simulated precipitate tests. Thus, it appears that the simulated and radioactive feeds behave similarly during the PHP.
The apparatus (Figure 3) was first tested using simulated nonradioactive feed. Figure 4 shows a test in the absence of HAN with high nitrite (1.0 M) feed. For this test, the apparatus was placed in a nonradioactive chemical hood. To obtain the necessary temperature, the reaction flask had to be covered with black insulating tape. Figure 4 was taken just after the 90°C heating cycle. As can be seen both the organic condensate and decanter solution are very dark. The decanter phase was red-orange. This color was most likely due to water soluble organics which formed in the reaction vessel and collected in the decanter. At the end of the reaction, the decanter solution was even darker than it appears in Figure 4. The organic condensate had separated into three distinct phases—an aqueous phase at the bottom, a dark organic phase in the middle and a lighter organic phase on top. The PHA was black with chunks of black solids which had settled.

The apparatus was then tested with simulated feed containing 0.01 M nitrite. This feed had been irradiated with cobalt-60 gamma rays. Figure 5 shows this test. This picture was taken after the reaction mixture had been heated to 100°C and most of the benzene had been collected. The organic product was orange, however, initially it was colorless. A majority of this phase is expected to be benzene. The orange is most likely due to higher boiling organics which do not get into the decanter until the reaction mixture is brought to a boil. About an equal amount of an aqueous phase was collected with the organic product. The aqueous phase in the decanter was clear with a small layer of what appears to be high-boiling organics on top. The precipitate hydrolysis aqueous (PHA) was a blue solution with a small amount of dark solids. By comparing Figure 4 and Figure 5 it can be seen that when the nitrite concentration was increased, all the respective solutions (condensate, decanter solution, and PHA) became darker presumably due to higher concentrations of organic compounds.

The apparatus was then put into the shielded cell. Figure 6 shows the apparatus and its associated feed bottle in Cell 3 of the SCO. This picture was taken through a three foot leaded glass window. Most of the other equipment shown in the picture is associated with the offgas system of a melter in an adjacent cell. Figure 7 is a close-up of the reprecipitated feed for one of the PHA tests. This was the low nitrite (0.01 M) feed resulting from the late wash process. This
Figure 4. Organic and Aqueous Condensate Phases during a High Nitrite (1M) Precipitate Hydrolysis Test Using Nonradioactive Unirradiated Precipitate.
Figure 5. Organic and Aqueous Condensate Phases during a Low Nitrite (0.01M) Precipitate Hydrolysis Test Using Nonradioactive Irradiated Precipitate (Gamma, Dose from Co-60 = 1.9E08 Rads).
Figure 4. Organic and Aqueous Condensate Phases during a High Nitrite (1M) Precipitate Hydrolysis Test Using Nonradioactive, Unirradiated Precipitate.
Figure 7. Washed Tank 48 Precipitate. Fresh Precipitate Is Floating while the Older Precipitate Has Settled.
picture was taken after the feed had settled overnight. It can be seen that there are two layers of precipitate. One is floating, and the other had settled to the bottom of the bottle. The floating layer would appear in a matter of minutes after mixing of the slurry had ceased. The bottom layer required several hours to settle. The floating layer was not present before the precipitate slurry was reprecipitated, for example, see Figure 1, confirming that this upper phase is fresh precipitate. The bottom layer was the original 9 year old precipitate that was in Tank 48. When the precipitate slurry was stirred, the upper phase foamed, while the lower precipitate only mixed with the supernate. When stirring was ceased and the lower precipitate had settled, the interface between the upper layer and slurry had not changed indicating that the upper layer was indeed floating and had foamed. These results are consistent with those observed with nonradioactive simulated slurries.5 Unirradiated simulants have had foaming problems that are not experienced when irradiated simulants are used. Such stratification can be expected to occur in any reprecipitated solution of radioactive KTPB slurry.

Figure 8 is a close-up of the decanter during a radioactive PHP test. This picture was taken when the mixture in the reaction vessel was boiling. The bubbles on top of the decanter water are boiling benzene. Although the water is condensed and falls back into the decanter, it is still apparently above the boiling temperature of benzene which is 80°C. At this temperature the benzene boils leaving behind only the higher boiling organics which may be the brown layer on top of the organic. Note that the color of the organic condensate is very light and that only about 1 mL of aqueous condensate has been collected.

Figure 9 shows the PHA from one of the radioactive precipitate hydrolysis tests. The PHA from the other test was identical to this. The solution was blue due to Cu^{2+} ions. A slight amount of brownish solids (presumably titanates) had settled to the bottom of the bottle. Both these solutions had the same appearance as the products from the hydrolysis of the simulated precipitate feed.

During the second radioactive test, gas compositions were measured using a gas chromatograph and sampling system identical to that used to detect hydrogen from the noble metal fission production decomposition of formic acid.11 In this PHP test, hydrogen concentrations up to 0.15 % and carbon dioxide concentrations as high as 20 % were detected. The results also indicated that another...
Figure 8. Organic and Aqueous Condensate Phases during a Low Nitrite (0.01M) Precipitate Hydrolysis Test Using Tank 48 Radioactive Precipitate (Gamma, Beta Dose from Cs-137 = 1.4E08 Rads).

Organic

Aqueous

Boiling Benzene
Figure 9. Aqueous Product from a Low Nitrite (0.01M) Precipitate Hydrolysis Test Using Tank 48 Radioactive Precipitate.
gas or gases were present. Unfortunately, this test developed a leak which prevented an accurate measure of the gas composition. The source of the leak has been eliminated and future PHP tests will measure the exact amounts of various gases produced. Carbon dioxide resulted from the reaction of formic acid and carbonates in the slurry. Hydrogen has been observed from the catalyzed decomposition of formic acid sorbed on copper metal.\textsuperscript{12} Hydrogen has been reported to form from noble metal catalyzed decomposition of formic acid.\textsuperscript{11,13} Lesser amounts have been observed in the presence of copper.\textsuperscript{14}

Although the complete results from analyses of the products are not available, these visual observations suggest that the PHP is the same for radioactive and simulated feeds. Other results indicate that the PHP was successful at hydrolyzing the K and Cs-137 tetraphenylboron in Tank 48 radioactive precipitate. This indication comes from mass balance calculations for both Cs-137 and K as well as B.

**Mass Balances for the Two PHP Tests**

Table 4 gives mass balances based on B, K, Ti, and Cs-137 for the first PHP test. Table 5 gives the results for the second. The amount fed was calculated from the composition of the precipitate (Table 2), the measured percent solids, and the amount of slurry used in the test. The values indicated as "recovered" are based on the final volumes of the PHA products and the measured concentrations in each PHA supernate such as that which is shown in Figure 9. Comparison of the fed and recovered values for both tests indicates that essentially all of the B, K, and Cs-137 has been solubilized into the PHA supernate. The agreement is much better in the second test probably because the amount fed was more carefully measured. In both tests the titanium recovery was low, as expected. The titanium remains insoluble as sodium titanate. The slight amount of solids in both PHA products will be analyzed for Ti as well as Sr-90, Pu, and U.
**Table 4.** B. K. Ti, and Cs-137 Mass Balances in the First Radioactive PHP Test

<table>
<thead>
<tr>
<th></th>
<th>B (g)</th>
<th>K (g)</th>
<th>Ti (g)</th>
<th>Cs-137 (mCi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount Fed&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.277</td>
<td>1.23</td>
<td>1.08</td>
<td>497</td>
</tr>
<tr>
<td>Amount Recovered&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.245</td>
<td>1.68</td>
<td>0.021</td>
<td>399</td>
</tr>
<tr>
<td>Recovery (%)</td>
<td>89</td>
<td>137</td>
<td>2.0</td>
<td>80</td>
</tr>
</tbody>
</table>

<sup>a</sup>Calculated from the volume fed (200 mL) and composition of feed (9.35% solids of composition given in Table 2).

<sup>b</sup>Calculated from the final volume (253 mL) and concentrations measured in solution.

**Table 5.** B. K. Ti, and Cs-137 Mass Balances in the Second Radioactive PHP Test

<table>
<thead>
<tr>
<th></th>
<th>B (g)</th>
<th>K (g)</th>
<th>Ti (g)</th>
<th>Cs-137 (mCi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount Fed&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.249</td>
<td>1.11</td>
<td>0.98</td>
<td>447</td>
</tr>
<tr>
<td>Amount Recovered&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.280</td>
<td>1.19</td>
<td>0.002</td>
<td>443</td>
</tr>
<tr>
<td>Recovery (%)</td>
<td>112</td>
<td>107</td>
<td>0.2</td>
<td>99.1</td>
</tr>
</tbody>
</table>

<sup>a</sup>Calculated from the volume fed (180 mL) and composition of feed (9.35% solids of composition given in Table 2).

<sup>b</sup>Calculated from the final volume (215 mL) and concentrations measured in solution.

**Final Product Volumes And Cs-137 Concentrations**

In each of the two radioactive tests four products were formed. These were the PHA, the aqueous phase left in the decanter, the organic condensate, and the aqueous condensate. Table 6 shows for each of the two runs the measured Cs-137 concentrations and the volumes for each of these products. The Cs-137 concentrations are given in Ci/gallon for comparison to the value of 24 Ci/gallon.
expected in the first precipitate feed for the DWPF. From Table 6, it is clear that the concentrations of Cs-137 in each of the organic condensates was considerably lower than in the feed. This was also true of the aqueous condensates and the aqueous phase left in the decanter. Even in this simple apparatus with one distillation stage, it appears that distillation nearly decontaminates the solution from Cs-137. The final Cs-137 concentrations in the organic condensates can be compared with 1000 dpm/ml which has been set as the limit for the organic stream leaving the DWPF. For the first test, the Cs-137 concentration was <10 dpm/mL and for the second it was 1.2 X 10^3 which is slightly higher than the limit. Based on the Cs-137 concentrations, the DF for Cs-137 in the organic condensates was >3 X 10^8 for the first test and 4 X 10^6 for the second. These large DF's suggest that decontamination will be successful in the DWPF where multiple separation stages are present.

Table 6. Measured Cs-137 Concentrations and Product Volumes in the Two Radioactive PHP Tests

<table>
<thead>
<tr>
<th></th>
<th>First Experiment</th>
<th>Second Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Cs-137] (Ci/gallon)</td>
<td>Volume (mL)</td>
</tr>
<tr>
<td>PHA</td>
<td>5.8</td>
<td>253</td>
</tr>
<tr>
<td>Decanter</td>
<td>0.0016</td>
<td>55</td>
</tr>
<tr>
<td>Aqueous Condensate</td>
<td>0.00015</td>
<td>3</td>
</tr>
<tr>
<td>Organic Condensate</td>
<td>&lt;2 x 10^-8</td>
<td>3</td>
</tr>
</tbody>
</table>

Preliminary ICP-MS analyses indicated that mercury was present in the decanter solutions and the aqueous condensates. It is known that mercury is in the waste resulting from the chemical separation processes at SRS. During the hydrolysis process, elemental mercury could have been formed and distilled from the reaction vessel as it is in the SRAT process. Also, diphenylmercury may be present in the
slurry as a product of radiolysis. More quantitative results will be presented in a later report.

Benzene Collected

The amount of benzene expected in each test can be calculated from the amount of slurry fed to the reactor and the weight percent TPB in the slurry given in Table 2. For the first test the calculated amount is 11 mL and for the second, 10 mL. The measured values were 3 and 11 mL respectively. In the second test it appears that essentially all the benzene was collected. In the first, 8 mL was lost. We currently have no explanation of why so much benzene was lost in the first test and not in the second. The temperature of the condensor was 15°C in both tests. The gas purge rate was nominally 2X higher in the second test; thus, one would think that more benzene would be lost in the second test. It may be that in the first test the complete hydrolysis of TPB and removal of aromatic from the PHA did not occur even though essentially all the Cs-137, K, and B were solubilized. In future tests the amount of aromatic organic remaining in the PHA will be measured using a liquid chromatographic method currently being developed. Also, in future tests we will put a benzene trap downstream from the condenser to ensure that all the benzene is collected.

CONCLUSIONS

The data presented in this report support the following conclusions.

1. There are no significant observable differences between the Cu catalyzed formic acid hydrolysis of radioactive TPB precipitates compared to simulated nonradioactive precipitates. Benzene is distilled from the reaction mixture and the PHA has a small amount of brown solids in it. It does remain to be shown that essentially all the aromatic compounds are distilled from the aqueous phase in the hydrolysis of the radioactive precipitates as they are in the hydrolysis of nonradioactive precipitates. This will be investigated in future tests when a liquid chromatograph is available that can analyze radioactive solutions.
2. Radioactive cesium and potassium TPB precipitates can be hydrolyzed by the current PHP even after the precipitate and slurry has been irradiated while being stored for several years in a precipitate hold tank. Essentially all Cs-137, K, and B are solubilized by the hydrolysis process.

3. In the ITP process, the Cs-137 will have to be reprecipitated from aged slurries due to the radiolysis of TPB while the slurry is being stored. This will produce fresh TPB precipitate which will float on the slurry and can cause foaming problems.

4. Benzene which is only slightly radioactive can be distilled from the radioactive PHP mixture. It appears that DF for Cs-137 may be higher than $10^6$ for this distillation.

5. Mercury present in the precipitate slurry is distilled from the reaction mixture during the hydrolysis. The form of this mercury will be investigated in future studies.

6. The fission products Rb-85 and Rb-87 are precipitated by TPB. Further Sr-90, U, and Pu are present in radioactive TPB precipitate presumably carried down by the sodium titanate. Other fission products may be present. Future studies will address this.

**FUTURE WORK**

Currently, work is under way to learn more about the hydrolysis of radioactive precipitate. These efforts include

- completing the analysis of feed and products from these two tests, including using ICP-MS to analyze for minor fission products and actinides

- expanding our ability to analyze organic species, especially in the PHA and organic condensate

- further characterizing the radioactive precipitate to determine the amount of Pu-239 and U-235 present

- refining the PHP apparatus to improve mass balance data, especially for the aromatic carbon compounds.
ACKNOWLEDGEMENTS

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REFERENCES


