CONF-930205--14

WSRC-MS--92-409

DE93 007954

DECOMPOSITION OF TETRAPHENYLBORATE PRECIPITATES USED TO ISOLATE Cs-137 FROM SAVANNAH RIVER SITE HIGH-LEVEL WASTE

by

D. M. Ferrara, N. E. Bibler, and B. C. Ha

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29802

Extended Summary of a Paper Proposed for Presentation at "WM '93 - HLW, LLW, Mixed Wastes and Environmental Restoration International Topical Meeting", February 28-March 4, 1993, Tucson, Arizona, and for Publication in the Proceedings

---

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P. O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401.

Available to the public from the National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

DECOMPOSITION OF TETRAPHENYLBORATE PRECIPITATES USED TO ISOLATE Cs-137 FROM SAVANNAH RIVER SITE HIGH-LEVEL WASTE

by

D. M. Ferrara, N. E. Bibler and B. C. Ha

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29802

ABSTRACT

This paper presents results of the radioactive demonstration of the Precipitate Hydrolysis Process (PHP) that will be performed in the Defense Waste Processing Facility (DWPF) at the Savannah River Site. The PHP destroys the tetraphenylborate precipitate that is used at SRS to isolate Cs-137 from caustic High-Level Waste (HLW) supernates. This process is necessary to decrease the amount of organic compounds going to the melter in the DWPF. Actual radioactive precipitate containing Cs-137 was used for this demonstration. Two tests were performed remotely in the shielded cells of Savannah River Technology Center (SRTC). A sample of the precipitate slurry was transferred to SRTC and adjusted to have a composition expected after the precipitate is washed in the SRS tank farm. These adjustments included reprecipitating the Cs-137 which had been released by radiolysis during long term storage of the slurry in the tank farm and washing the precipitate to achieve a nitrite concentration of 0.01M. 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 nonradioactive precipitates. The main product of the hydrolysis is benzene. In the radioactive tests, 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. Hg that was in the waste was also distilled from radioactive reaction mixture.

INTRODUCTION

The 130 million liters of radioactive waste currently stored in the Savannah River Site (SRS) consists of caustic sludges and supernates. After treating the wastes, radionuclides from the sludges and supernates will be immobilized into a borosilicate glass at the Defense Waste Processing Facility (DWPF).[1] Before vitrification, the soluble radionuclides have to be removed from the supernate. Cs-137 will be removed by precipitating it with tetraphenylborate (TPB) precipitate. Other radionuclides will be removed by adsorbing them on sodium titanate. This process was successfully demonstrated using the In-Tank Precipitation (ITP) process at the SRS Tank Farm in April 1983.[2]

To keep the organic material from being fed to the DWPF melter, the CsTPB precipitate will be treated to remove the organic portion of the TPB precipitate. The Precipitate Hydrolysis Process (PHP) was developed to hydrolyze the TPB using formic acid in the presence of a copper catalyst. The products of this hydrolysis are benzene, and an aqueous solution containing $^{137}Cs^+$, BO_3^{3-} and K^+ ions.

The purpose of this radioactive study was to evaluate the PHP with actual radioactive TPB slurry generated during the ITP demonstration in Tank 48 of the SRS tank farm.[2] This demonstration, performed in 1983, indicated that precipitation could be used to isolate Cs-137 from the supernate. The demonstration generated twenty thousand gallons of precipitate slurry. Of this slurry, 1.4 L was sent to SRTC. Approximately 0.7 L of the highly radioactive precipitate slurry from the ITP process[4] in Tank 48 was used for these tests. The ITP demonstration was completed in April 1983. Based on the concentration of Cs-137 present (approximately 4 Ci/gal) the slurry had received a dose of approximately 1.4×10^8 rad by April 1992 when the PHP tests started.

At the time of this study, the slurry from the ITP demonstration had aged for nine years, and Cs-137 had been solubilized after some of the TPB precipitate had been destroyed by radiolysis. To prepare for the PHP, the slurry was reprecipitated and washed so it could be fed to the PHP had the same NO_2^-, NO_3^-, Na^+, OH^-, and solid concentrations as slurries expected from late washing process.[3] Two PHP tests were performed using this washed Tank 48 radioactive slurry.

EXPERIMENTAL

The original 0.7 L sample was then was then washed as it would be in the late wash process.[4] Inhibited water similar to that used in the Tank Farm (0.015 M NaOH) was used in the wash process.

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 SRTC Shielded Cells Operations (SCO) personnel. The reaction took place in a reaction vessel on a hot plate at between 92°C and boiling. Mounted on top of the reaction vessel was a condenser. A decanter was used between the condenser and the reaction vessel to divert the organic condensate to a sample vessel and collect a small fraction of the aqueous condensate. The condenser was kept at 15°C to condense the benzene and steam. The procedure used is summarized in Table I. This procedure is identical to that used in larger scale studies with nonradioactive precipitate slurries.[5,6]

Table I. Procedures for the Radioactive Precipitate Hydrolysis Tests in the Absence of HAN[a]

- 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.

---

[a] Taken from reference 5.

After each test, the aqueous product, the aqueous and organic condensates, and the small amount of the aqueous solution which collected beneath the organic condensate were sampled for analysis. 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 were removed without dilution.

RESULTS AND DISCUSSION

Reprecipitation of the Cs-137 and Washing the Precipitate

Since the slurry was approximately nine years old, sufficient radiolysis had occurred to destroy some of the TPB and solubilize Cs-137 and K^+ to the supernate. Consequently, fresh NaTPB was added to the supernate to reprecipitate this Cs-137 and K^+. The precipitate was then washed to dilute the NO_2^- and Na^+ to the levels expected in the late wash flowsheet at SRS.[7] Concentrations in the initial and final solutions in this reprecipitation and wash process are shown in Table II. The final concentration of Na^+, NO_2^-, and NO_3^- are comparable the those expected in the late wash flowsheet. After washing, the Na^+, B, NO_2^-, NO_3^-, and Cs-137 concentrations had decreased by factors in the range of 20 to 30 while K^+ had decreased by a factor of 70. The decrease in Na^+, B, NO_2^-, and NO_3^- are due mostly to washing and dilution of the supernate while those for K^+ and Cs-137 also resulted from the reprecipitation.

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

	Moles/Liter					µCi/g
	NO_2^-	NO_3^-	Na^+	K^+	B^b	Cs-137
9 Year Old Slurry Supernate	0.38	0.042	3.8^a	0.014	0.052	37
Washed $Slurry^c$	0.011	0.002	0.12	0.0002	0.0032	1.3

---

[a] The high concentration of sodium is due to NaOH added to Tank 48 to inhibit corrosion.

[b] Soluble boron resulting from radiolysis of TPB.

[c] 0.39 L of 9.35 weight percent solids.

Composition of the TPB Precipitate

The composition of the washed TPB precipitate is given in Table III. This composition is given as the weight percent of solids resulting from drying an aliquot of the slurry at 110°C. Note that on a molar basis the K, B, 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.

Table III. Composition of KTPB Precipitate in the PHP Feed Slurry

	Weight Percent	mCi/g	Moles/100 g
B	1.41 ± 0.08	-----	0.13
K	6.28 ± 0.54	-----	0.16
TPB^-	0.3 ± 0.96	-----	0.16
Ti	5.53 ± 0.31	-----	-----
Cs-137	-----	25.3 ± 1.1	-----

---

[a] Average of duplicate analyses
[b] Average of triplicate analyses

Ti made up 5.53 weight percent of the solids. Sodium titanate ($NaTi_2O_4$) was added to Tank 48 to remove residual traces of Sr-90 and Pu from the supernate. Assuming the Ti was present as $NaTi_2O_4$, the Ti compound would make up 11.5 weight percent of the solids. This is about twice the expected concentration in the feed to the DWPF salt cell.[8] The difference may be due to the technique used to sample the precipitate in Tank 48.

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 nonradioactive precipitate feeds, suggesting the nonradioactive and radioactive feeds behave similarly during the PHP.

The low nitrite (0.01 M) feed resulting from the late wash process originally had two layers of precipitate; one floating and the other settled on 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 reprecipitation. 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. These results are consistent with those observed with nonradioactive simulated slurries.[6] 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.

The PHA solutions from the radioactive precipitate hydrolysis tests were blue due to Cu^{2+} ions. A slight amount of brownish solids (presumably titanates) 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.[8]

These visual observations suggest that the PHP is the same for radioactive and simulated feeds.

Elemental Analyses in the Product Streams

Several soluble ions were found in the PHA supernate. Concentrations of several soluble elements in the PHA and the aqueous decanter solution are listed in Table IV.

Table IV. Concentrations (ppm) of Soluble Elements

Element	First PHP Test		Second PHP Test	
	PHA	Aqueous Condensate	PHA	Aqueous Condensate
K	6470	1.5	5520	0.48
Na	2850	8.6	3370	7.1
Cu	1040	0.27	1070	0.076
B	950	1.5	1300	1.3
Zn	950	4.2	260	1.8
Ca	170	35	170	22
Ti	83	0.004	9.8	0.014
Mg	52	0.44	60	0.35
Fe	27	0.11	42	0.13
Si	14	5.8	56	11
Ba	8.4	0.24	17	0.26
Hg	5.6	1328	3.8	800
Mn	4.2	0.012	8.4	0.06
Cs-137[a]	5.8	0.0016	7.8	0.00046

---

[a] Results are in units of Ci/gal.

K is precipitated along with the Cs from the high-level waste salt solution during ITP. The K and Cs are then released to the supernate when the TPB is destroyed by hydrolysis. The K concentration in the supernate of the washed Tank 48 precipitate feed was only 58 ppm. The concentrations of K in the PHA's and the aqueous decanter solutions from each of the tests are presented in Table IV. The concentrations of K in the PHA's were very similar to the concentration in PHA produced from the nonradioactive study.[8]

Cu is used to catalyze the reaction. If the Cu concentration is too high, it can complicate the vitrification process and precipitate in the final glass. Previous nonradioactive tests with Co-60 irradiated precipitate indicated the concentration of Cu in the PHA should be in the range from 850 to 1050 ppm to mitigate these complications. Table IV includes Cu concentrations in the PHA from the Tank 48 radioactive precipitate feed hydrolysis. These results indicate that the Cu concentrations (1040 ppm in the first test and 1070 ppm in the second) were very close to the high end of the range established in the studies with nonradioactive slurries.

Hg is present in the waste from chemical processing steps at SRS. In addition to removing benzene from the precipitate feed, the PHP was designed to remove mercury from the aqueous stream. Hg is believed to be present in the tetraphenylborate feed primarily as diphenylmercury as a result of reactions in the tank. During the PHP, diphenylmercury is reduced to elemental Hg and collected in the aqueous decanter solution.

Concentrations of Hg in the aqueous products of the PHP are given in Table V. The Hg concentration in the washed Tank 48 precipitate feed was 723 ppm. Benzene products were essentially free of Hg (< 0.3 ppm). The Hg concentrations in the PHA solutions were only at 5.6 and 3.8 ppm in the two tests. The low Hg concentrations in the PHA and organic products suggest the PHP was successful in reducing the diphenylmercury to elemental Hg, and distilling it from the PHA to the aqueous decanter solution.

Table V. Hg Concentrations Measured in the PHP Products[a]

	First PHP Test	**Second PHP Test**
PHA	5.6 ppm	3.8 ppm
Organic Condensate	< 0.3 ppm	< 0.3 ppm
Decanter Solution[b]	1328 ± 56 ppm	800 ± 38 ppm

---

[a] Feed concentration = 723 ppm

[b] The deviations indicated are standard deviations of three analyses.

Final Product Volumes And Cs-137 Concentrations

In both tests, four product solutions were collected. These were the PHA, organic condensate, aqueous condensate, and an aqueous carryover which collected beneath the organic condensate in the decanter. Table VI shows the measured Cs-

137 concentration and the volumes of each product for the two tests.

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

	First Test		Second Test	
	Product Volume (mL)	[Cs-137] (Ci/gallon)	Product Volume (mL)	[Cs-137] (Ci/gallon)
PHA	253	5.8	215	7.8
Aqueous Condensate	55	0.0016	55	0.00046
Aqueous Carryover	3	0.00015	2	0.00029
Organic Condensate	3	$<2 \times 10^{-8}$	11	2.1×10^{-6}

The Cs-137 concentration expected in the first precipitate feed for the DWPF is 24 Ci/gallon. Clearly, 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 phases in contact with the organic condensate. Even in this simple apparatus with one distillation stage, it appears that distillation nearly decontaminates the organic 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 1.2×10^3 which is slightly higher than the limit. These results suggest that decontamination will be successful in the DWPF.

Mass Balances for the Two PHP Tests

Table VII gives mass balances based on B, K, Ti, and Cs-137 for the first PHP test. Table VIII gives the results for the second. Comparison of the fed and recovered values for both tests indicates 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 Ti recovery was low, as expected. The Ti remains insoluble as $NaTi_2O_4$. The mass balances indicate that the PHP was successful in solubilizing all the B, K and Cs-137.

Table VII. B, K, Ti, and Cs-137 Mass Balances in the First Radioactive PHP Test

	B	**K**	**Ti**	**Cs-137**
Amount Fed[a]	0.277 g	1.23 g	1.08 g	497 mCi
Amount Recovered[b]	0.245 g	1.68 g	0.021 g	399 mCi
Recovery (%)	89	137	2.0	80

---

[a] Calculated from the volume fed (200 mL) and composition of feed (9.35% solids of composition given in Table I).

[b] Calculated from the final volume (235 mL) and concentrations measured in solution.

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

	B	**K**	**Ti**	**Cs-137**
Amount Fed[a]	0.249 g	1.11 g	0.98 g	447 mCi
Amount Recovered[b]	0.280 g	1.19 g	0.002 g	443 mCi
Recovery (%)	112	107	0.2	99

---

[a] Calculated from the volume fed (200 mL) and composition of feed (9.35% solids of composition given in Table I).

[b] calculated from the final volume (235 mL) and concentrations measured in solution.

CONCLUSIONS

Results indicated the precipitate hydrolysis of Tank 48 radioactive precipitate slurry using the late wash flowsheet was successful. Results of the tests support the following conclusions with respect to hydrolysis of Tank 48 precipitate slurry:

- 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.

- Radioactive Cs and K 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.

- 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.

- Hg was successfully reduced and stripped from the precipitate feed into the aqueous decanter solution. No mercury was found in the organic product. The concentration of Hg in the PHA was very low (< 6 ppm).

- 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.

ACKNOWLEDGMENTS

The authors would like to thank the personnel of the SRTC Shielded Cells Operations. We are especially grateful for the work of R. W. Blessing, J. T. Mills and R. H. Galloway. Their outstanding skill at operating the master-slave manipulators were essential to completing these tests. We would also like to thank D. M. Marsh for her technical support.

REFERENCES

1. *DWPF Process and Equipment Description*. USDOE Report DPSOP 257-1, Savannah River Site, Aiken, SC 29808 (1988).

2. E. B. Snell and C. J. Heng. *Salt Decontamination Demonstration Test Results*. USDOE Report DPSP-83-17-8, Savannah River Site, Aiken, SC 29808 (1983).

3. D. L. Fish. *Initial Technical Bases-DWPF Late Washing Facility* (U). USDOE Report WSRC-RP-92-793, Savannah River Site, Aiken, SC 29808 (1992).

4. E. B. Snell and C. J. Heng. *Salt Decontamination Demonstration Test Results*. USDOE Report DPSP-83-17-8, Savannah River Site, Aiken, SC 29808 (1983).

5. L. F. Landon. *DWPF Integrated Cold Runs, Revised Technical Bases for Precipitate Hydrolysis (U)*. USDOE Report WSRC-RP-92-737, Savannah River Site, Aiken, SC 29808 (1992).

6, *Sodium Peroxide Fusion Dissolution of Glass for Elemental Analysis*. DWPF Standard Operating Procedure 221-S-7011, Savannah River Site, Aiken, SC 29808 (1992).

7. D. L. Fish. *Initial Technical Bases-DWPF Late Washing Facility (U)*. USDOE Report WSRC-RP-92-793, Savannah River Site, Aiken, SC 29808 (1992).

8. Data Presented by J. C. Marek, *Late Washing and Low Nitrite Precipitate Hydrolysis,* Presented to the Westinghouse Independent Technical Review Board, June 19, 1992.

END

DATE FILMED

9/23/93