Radioactive Testing Results in Support of the In-Tank Precipitation Facility - Filtrate Test

by

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Radioactive Testing Results in Support of the In-Tank Precipitation Facility - Filtrate Test

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Summary

Decomposition of excess sodium tetraphenylborate (NaTPB) occurred at a much slower rate with the filtrate from actual waste Test 4A than with the original slurry in Test 4A. Based on the rate of 3PB formation, a benzene (C_6H_6) generation rate of 0.027 mg C_6H_6 /L-h is determined over the 647-hour test period for the Filtrate Test. Previously, the Test 4A slurry exhibited a benzene generation rate of 15 mg C_6H_6 /L-h and consumed all excess NaTPB as well as a fraction of the potassium and cesium tetraphenylborate (K/Cs-TPB) solids. The lack of reactivity for the NaTPB likely results from the reduced concentrations of metals, and possibly palladium, from filtration. Because experimental uncertainty in analyses indicates palladium could well be at or near the same concentration as that in the reactive Test 4A slurry, a synergistic activation of the palladium by other metals may be the source of increased reactivity in the earlier study with Test 4A slurry. Based on analysis of the Filtrate Test solution and comparison with calculated concentration for the Test 4A slurry, unchanged elemental components included Ca, Mg, Mo, Na, Pd, U and W and lower components included Ag, Al, Au, Cd, Ce, Cr, Cu, Fe, Hg, La, Mn, Pb, Pt, Rh, Ru, Si, Sn, Ti, Zn and Zr. Changes in the following elements proved indeterminate: As, B, Ba, Co, Ir, Li, Os, P, Se, Sr, and V.

Introduction

The In-Tank Precipitation (ITP) facility initiated radioactive operation in August, 1995. During pump operation in December 1995, benzene evolution from Tank 48H exceeded expectations, although the vapor phase benzene concentration never approached the operational safety limit. Subsequent investigations revealed catalytic decomposition of excess sodium tetraphenylborate produced the benzene [1].

The Defense Nuclear Facilities Safety Board (DNFSB) issued Recommendation 96-1[2] suggesting suspension of ITP operations pending an improved understanding for the mechanisms of benzene generation, retention and release. The Department of Energy developed a plan to resolve the issues raised by the DNFSB based on a revised safety strategy and a combination of bench, pilot and plant-scale tests [3]. The implementation plan includes bench-scale tests using radioactive waste to confirm that benzene generation rates using simulants bound the next three planned batches of Cycle 1. This report documents results investigating the decomposition of excess NaTPB in presence of filtrate from one the Cycle 1 Demonstration tests, fulfilling a request by CST Engineering and the ITP Flow Sheet Team [4].

Experimental

Filtrate (40-mL) from the Cycle 1 Demonstration, Test 4A, was placed in a clean polyethylene bottle (PE) containing a magnetic stirring bar. The Test 4A filtrate previously had been stored at ambient laboratory temperature in a PE bottle for 54 days after filtering the Test 4A slurry through a 0.45- μ m pore size cellulose nitrate disposable filter. The calculated solution composition of the filtrate for sodium, hydroxide, nitrate and nitrite is provided in Table I. Sodium tetraphenylborate solution (1.918 g, Holly Oak NaTPB solution, sample ID L9768-35) was added and the resulting mixture stirred for 75 minutes at ambient laboratory temperature. The NaTPB added was sufficient to precipitate all of the cesium and potassium – based upon previous analyses of the filtrate

-- and provide a NaTPB concentration of 0.02 molar. The bottle was removed from the magnetic stirrer and placed in a waterbath heated to $45 \pm 1^\circ\text{C}$. The bottle was agitated briefly once daily except on weekends during the test.

Table I. Calculated Composition of Test 4A Filtrate

<u>Analyte</u>	<u>Concentration (M)</u>
Sodium	5.0
Hydroxide	2.1
Nitrate	1.6
Nitrite	0.69

Periodically, 1-2 mL of slurry were removed from the bottle and filtered using a syringe filter with 0.20- μm pore size (Gelman Acrodisc #4496 – Nylon membrane). The filtrate was analyzed by high performance liquid chromatography (HPLC) for the determination of sodium tetrphenylborate (NaTPB), triphenylborane (3PB), diphenylborinic acid (2PB), phenylboronic acid (1PB) and phenol concentrations. At the conclusion of the test, the remainder of the reaction slurry was filtered through a 0.20- μm pore size disposable filter (Nalgene – cellulose nitrate membrane). Duplicate subsamples of the filtrate were analyzed by inductively coupled plasma emission spectroscopy (ICP-ES) and inductively coupled plasma mass spectroscopy (ICP-MS) to determine a wide range of elemental concentrations and isotopic abundances.

Results and Discussion

White solids were clearly visible in the reaction bottle immediately upon addition of the NaTPB solution and throughout the testing period. After 3 hours at 45°C (4.25 hours after NaTPB addition), gamma pulse height analysis indicated radioactive cesium-137 removal from the liquid phase to a level of 0.45 nCi/g, which is well below the limit of 45 nCi/g allowed for transfer of decontaminated salt solution to Saltstone [5].

Table II provides the concentrations of NaTPB, 3PB, 2PB, 1PB and phenol for the Filtrate Test and control samples. Figure 1 provides a plot of the Filtrate Test data versus time. The concentration of soluble NaTPB was low throughout the test due to the high sodium ion concentration. The concentrations of 3PB and phenol increased during the test period. Detectable amounts of 2PB appeared only at the end of the test period, whereas 1PB exhibited no change. These findings suggest a very slow NaTPB decomposition rate.

Based on the rate of 3PB formation, a benzene (C_6H_6) generation rate of 0.027-mg $\text{C}_6\text{H}_6/\text{L-h}$ is determined over the 647-hour test period. Previously, the Test 4A slurry exhibited a benzene generation rate of 15-mg $\text{C}_6\text{H}_6/\text{L-h}$ and consumed all excess NaTPB as well as a fraction of the potassium and cesium tetrphenylborate (K/Cs-TPB) solids [6]. Clearly, the rate of NaTPB decomposition is slower in the Filtrate Test than in Test 4A. Differences between Filtrate Test and Test 4A include:

- the presence of sludge solids in Test 4A ($790 \pm 82 \text{ mg/L}$), but none in the Filtrate Test,

- a higher excess of NaTPB in the Filtrate Test (0.020 M) versus Test 4A (0.011 M),
- higher concentrations of intermediates, except 2PB in the Filtrate Test compared to Test 4A,
- Test 4A conducted in carbon steel vessel versus PE for the Filtrate Test,
- Test 4A sealed under air and sampled with syringe through a rubber septum, whereas the Filtrate Test conducted in a closed bottle under air with the bottle opened periodically to the air during sampling, and
- Test 4A conducted at much higher radiation dose rate (1030 rad/h) than the Filtrate Test (estimated at 17 rad/h)¹.

The low reactivity of the excess NaTPB is not attributed to the higher excess of NaTPB since previous testing showed the decomposition rate of NaTPB is independent of concentration [6-8]. The low reactivity does not result from the low radiation dose rate since catalytic NaTPB decomposition occurs in the absence of radiation [7-9]. PE bottles have not been routinely used in more recent testing due to the possible removal of benzene by sorption into the vessel walls. However, rapid NaTPB decomposition has been observed in tests conducted in PE bottles as well as glass and carbon steel vessels [7-10] and, therefore, the low reactivity in this test is not attributed to the PE vessel material.

Depletion of oxygen or oxygenating species in the liquid phase is believed necessary to activate the catalyst and initiate the rapid decomposition of NaTPB. Oxygen was present initially in both tests as both were sealed under an air atmosphere with no attempts to remove dissolved oxygen. Furthermore, there were no attempts to exclude or remove oxygen during sampling. Air is assumed to leak into the sealed carbon steel vessels during or after sampling to replace the volume of slurry removed.

The headspace in Test 4A initiated at about 40 mL or 40% of the total slurry volume and increased during the test as slurry samples were removed. The headspace in the Filtrate Test initiated at about 22 mL or 52% of the total slurry volume. Although the initial concentrations of intermediates are higher in the Filtrate Test, the total initial quantities of intermediates were similar for both tests. Since Test 4A had a larger vapor volume, the molar ratio of oxygen to intermediates is about twice that in the Filtrate Test. These differences do not appear significant enough to explain the different reaction rates.

The low reactivity of the excess NaTPB in the Filtrate Test is attributed primarily to the removal of the sludge solids. Filtering the Test 4A slurry removed the sludge solids and, consequently, the insoluble metallic components of the sludge. Table III provides a list of the elemental and isotopic composition of the final filtered test solution (excess NaTPB solids removed). Included for comparison are the calculated minimum, average and maximum elemental concentrations of the Test 4A slurry. The solution for the Filtrate Test was obtained from this slurry.

¹ Internal dose rate estimated from Cs-137 activities using same methodology reported in D. D. Walker and J.P. Doherty, "Effects of Gamma Irradiation on the Rheology of KTPB Slurries," DPST-85-926, November 5, 1985.

Based on analysis of the Filtrate Test solution and comparison with calculated values for the Test 4A slurry, metal components with insignificant changes in concentration included Ca, Mg, Mo, Na, Pd, and W. The concentrations of numerous components decreased in the filtrate relative to the parent slurry, including Ag, Al, Au, Cd, Ce, Cr, Cu, Fe, Hg, La, Mn, Pb, Pt, Rh, Ru, Si, Sn, Ti, Zn and Zr. The change in concentration for the elements: As, B, Ba, Co, Ir, Li, Os, P, Se, Sr, and V was indeterminate, as these elements were not analyzed for in either the Test 4A slurry or the Filtrate Test solution.

Unchanged concentrations for sodium and molybdenum are not unexpected, since sodium is very soluble and molybdenum, present as molybdate, is commonly found in filtered radioactive waste [6]. Calcium and magnesium are also commonly found in radioactive waste and are relatively low insolubility due to the presence of carbonate, sulfate and phosphate [11]. Since tungsten appears unchanged, we conclude that tungsten is present in the original Test 4A slurry primarily as a soluble tungstate, which is consistent with properties comparable to molybdenum. Most of the metals present in the Test 4A slurry are not present in the Filtrate Test filtrate. This is consistent with the removal of sludge solids by filtration. The bulk of the metals present in the Test 4A slurry derives from sludge solids.

Palladium was detected in both Filtrate Test samples with an average concentration of $5.19 \pm 3.46 \text{ E-02 mg/L}$ (see Table II). One of the results (2.74E-02 mg/L) is just above the minimum quantifiable limit (2.00E-02 mg/L) for the analytical method. Because of the large standard deviation for the results, the lower 95% confidence limit for palladium is below the quantifiable limit of the analytical method. However, since palladium was detected in both samples, palladium is likely present in the Filtrate Test. The average concentration of palladium in the Filtrate Test was 56% of the calculated average for the Test 4A slurry suggesting some removal of palladium by filtration. However, there is considerable overlap in the confidence intervals and, therefore, one cannot conclude with high confidence that the palladium concentration is lower in the Filtrate Test than in Test 4A.

Palladium is known to catalyze the decomposition of NaTPB in alkaline slurries [7-9]. Since a rapid NaTPB decomposition rate was observed in the Test 4A slurry, but not in the Filtrate Test, we conclude that palladium was either not present in sufficient concentration (i.e., near zero) or not in an active form. Perhaps the removal of the metals present in the sludge solids (e.g., Cu and Hg) prevented the formation of an active catalyst form in the Filtrate Test.

Platinum has also been reported to catalyze the chemical decomposition of NaTPB². The calculated platinum concentration in the Test 4A slurry ranged from 1.63 to 31.1 $\mu\text{g/L}$ (see Table II). Platinum was below the quantifiable limit in the Filtrate Test filtrate. Therefore, the lack of NaTPB reactivity may also be the result of reduced platinum content.

² Preliminary results reported by Y. Su (PNNL) from work funded by DOE EMSP Basic Sciences grant.

Table II. HPLC Analytical Results for the Radioactive Filtrate Test and Control Samples

Sample ID	4AFIL-1	4AFIL-2	4AFIL-3	4AFIL-4	4AFIL-5	4AFIL-6	4AFIL-7
Date & Time	3/3/98 1200	3/5/98 1200	3/9/98 1200	3/12/98 0800	3/16/98 0800	3/23/98 0800	3/30/98 0800
Elapsed Time (h)	3	51	147	215	311	479	647
ADS #	3-105340	3-105516	3-105682	3-105798	3-105988	3-106283	3-106575
Cs-137 (nCi/g)	4.48E-01	nd	nd	nd	nd	nd	nd
NaTPB (mg/L)	<10	<10	<10	<10	<10	10	13
3PB (mg/L)	108	132	134	138	143	147	163
2PB (mg/L)	<10	<10	<10	<10	<10	10	10
1PB (mg/L)	36	31	34	33	33	37	34
Phenol (mg/L)	864	744	975	1001	1049	1042	1096
Control Sample							
ADS #	3-10534	3-105517	3-105683	3-105799	3-105989	3-106284	3-106576
NaTPB (mg/L)	111	112	115	112	114	111	109
3PB (mg/L)	93	93	95	95	95	93	89
2PB (mg/L)	103	104	105	108	102	101	100
1PB (mg/L)	89	78	105	101	98	105	100
Phenol (mg/L)	274	238	315	316	314	326	308

nd = not determined

Figure 1. Plot of the NaTPB, 3PB, 2PB, 1PB and Phenol Concentrations versus Time in the Radioactive Filtrate Test

Table III. Elemental and Isotopic Composition of Filtrate Test Solution and Test 4A Slurry

		Filtrate Test	Filtrate Test	Filtrate Test	Filtrate Test	Test 4A	Test 4A	Test 4A
		ICP-ES	ICP-ES	ICP-MS	ICP-MS	Slurry	Slurry	Slurry
	Units	Average	Std. Dev.	Average	Std. Dev.	Minimum	Average	Maximum
Ag	mg/L			8.88E-02	2.23E-02	2.29E-01	1.09E+00	2.06E+00
Al	mg/L	7.06E+03	4.82E+01			7.66E+03	7.69E+03	7.71E+03
As	mg/L					1.56E+00	1.89E+00	2.21E+00
Au	mg/L			0	0	7.29E-04	1.62E-03	3.14E-03
B	mg/L	3.95E+02	5.22E+01					
Ba	mg/L <	5.27E+00	1.19E-02					
Ca	mg/L	3.12E+01	5.15E+00			1.79E+01	3.10E+01	4.52E+01
Cd	mg/L <	2.45E+00	5.53E-03	0	0	4.24E-01	1.06E+00	1.73E+00
Ce	mg/L			2.91E-01	0.00E+00	7.75E+00	1.09E+01	1.41E+01
Co	mg/L <	8.49E+00	1.91E-02			8.45E-02	1.15E-01	1.52E-01
Cr	mg/L	6.72E+01	2.07E+00			1.09E+02	1.21E+02	1.34E+02
Cu	mg/L <	3.98E+00	8.98E-03			8.62E+00	1.59E+01	2.33E+01
Fe	mg/L <	1.76E+01	1.63E+01			4.74E+01	6.87E+01	9.01E+01
Hg	mg/L			3.40E-02	1.19E-02	3.45E+01	4.34E+01	5.23E+01
Ir	mg/L			0	0	0.00E+00	7.07E-04	2.62E-03
La	mg/L <	1.73E+01	3.91E-02	7.47E-02	4.53E-02	1.35E+00	1.94E+00	2.57E+00
Li	mg/L <	1.07E+02	2.40E-01					
Mg	mg/L	4.53E+00	1.77E+00			1.60E+00	2.62E+00	3.65E+00
Mn	mg/L <	1.87E+00	4.21E-03			2.59E+01	2.93E+01	3.27E+01
Mo	mg/L	3.53E+01	1.95E+00	4.05E+01	2.14E+00	3.30E+01	3.80E+01	4.30E+01
Na	mg/L	1.16E+05	8.97E+02				1.15E+05	
Ni	mg/L <	1.13E+01	2.56E-02			1.17E+01	1.72E+01	2.27E+01
Os	mg/L			0	0	0.00E+00	2.32E-03	1.00E-02
P	mg/L	7.90E+01	6.12E+00					
Pb	mg/L <	3.49E+01	7.87E-02	4.07E-01	4.36E-02	3.16E+00	4.55E+00	5.94E+00
Pd	mg/L			5.19E-02	3.46E-02	3.94E-02	9.25E-02	1.59E-01
Pt	mg/L			0	0	1.63E-03	9.64E-03	3.11E-02
Re	mg/L			0	0	1.48E-03	2.12E-03	2.79E-03
Rh	mg/L			6.50E-01	3.88E-02	1.14E+00	1.26E+00	1.39E+00
Ru	mg/L			1.16E+00	1.49E-01	2.55E+00	3.07E+00	3.67E+00
Se	mg/L					2.42E+00	4.49E+00	7.80E+00
Si	mg/L <	7.71E+01	1.74E-01			1.09E+01	2.48E+01	3.87E+01
Sn	mg/L <	1.08E+01	2.44E-02	1.41E+00	4.72E-02	2.82E+00	3.45E+00	4.09E+00
Sr	mg/L <	2.02E+00	4.56E-03			6.56E-01	1.13E+00	1.60E+00
Ti	mg/L <	8.09E+00	1.82E-02			6.25E+01	6.51E+01	6.77E+01
V	mg/L <	9.44E+00	2.13E-02			1.73E+00	2.75E+00	3.81E+00
W	mg/L			7.28E-01	6.84E-02	4.81E-01	7.39E-01	9.99E-01
Zn	mg/L	7.25E+00	7.71E-01			8.94E+00	9.74E+00	1.05E+01
Zr	mg/L <	1.17E+01	2.64E-02	2.16E-01	0.00E+00	3.21E+00	6.32E+00	9.50E+00
Tc-99	mg/L			8.40E+00	4.28E-01			
U-235	mg/L			1.92E-01	1.97E-02			
U-238	mg/L			3.57E+00	4.75E-01			
Total U	mg/L			3.91E+00	4.95E-01	3.62E+00	5.59E+00	7.79E+00
Np-237	mg/L			0	0			
Pu-239	mg/L			0	0			

0 value indicates below detection limit

Quality Assurance

This work used the following task plans.

M. J. Barnes and D. T. Hobbs, "Task Technical Plan for Radioactive Tests in Support of the In-Tank Precipitation Facility," WSRC-RP-97-0059, revision 1, November 26, 1997.

D. D. Walker and D. T. Hobbs, "Task Quality Assurance Plan for Radioactive Tests in Support of the In-Tank Precipitation Facility," WSRC-RP-97-0060, revision 0, April 18, 1997.

This document, with Reference 6, completes the work requested in the authorizing task request.

J. E. Marra and J. T. Carter, "Technical Task Request (U), Actual Waste Studies for DNFSB 96-1, HLE-TTR-97014, November 14, 1996.

Daily experimental conditions and operations are recorded in the laboratory notebook WSRC-NB-98-00074. All analyses performed by the Analytical Development Section except those using HPLC methods were performed as routine samples and used controls specified by ADS procedures. A control sample consisting of known concentrations of reagent grade NaTPB, 3PB, 2PB, 1PB and phenol dissolved in water was submitted with each set of radioactive testing samples. Analytical results for the control sample indicated no corrections are needed over the course of the tests for systematic variances in the responses measured for the control sample.

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