Characterization of Tank 49H Solids

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DOE Contract No. DE-AC09-96SR18500

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June 8, 1999

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Summary

Tank 49H contains wash water from the 1983 demonstration of the In-Tank Precipitation Process. Over the last several months, SRTC helped study the decomposition of sodium and potassium tetraphenylborate present within the tank. Video examination of the tank contents showed a thin layer of solids floating on the liquid. Characterization of samples of these solids provide the following conclusions.

- The samples suggest that the layer contain predominantly inorganic salts (> 95 wt %).
- Samples from the surface layer contain several different solid compounds with compositions differing sharply for samples collected by different methods.
- Compounds identified in the solid layer include sodium nitrate, sodium nitrite, sodium carbonate, sodium bicarbonate, sodium aluminosilicate, and titanium dioxide
- Analyses of the organic constituents of samples from Tank 49H showed minute (~1 wt %) quantities of tetraphenylborate and terphenyls.
- Data from the solids analyses do not suggest the presence of large quantities of biphenyl. The analyses do not help to explain the discrepancy between measured benzene emissions and predicted benzene formation based on phenylborate compound concentrations measured in liquid samples.
- Calorimetric analysis of the solids indicates the materials will not combust at temperatures below 300 °C.

Introduction

The contents of Tank 49H originated from waste water generated during the 1983 demonstration of the In-Tank Precipitation process.¹ The matrix contains small quantities of sodium and potassium tetraphenylborate. Sample analyses as recent as November of 1992 showed the tank contained 0.28 M free hydroxide.² Continued operation of Tank 49H in air-based mode caused the pH to drop due to carbonate absorption. Facility personnel observed elevated benzene generation rates on August 4, 1998, during a planned outage of the ventilation system. Engineering declared a Potential Inadequacy in the Safety Analysis (PISA). Subsequent investigation identified the cause as tetraphenylborate decomposition caused primarily by the loss of free hydroxide.³ SRTC personnel analyzed liquid and vapor space samples for phenylborate and benzene, respectively. Regression of the data indicated the decomposition rate of sodium tetraphenylborate exceeded that defined in the safety documentation. Additionally,

during November Engineering elected to inert the vapor space of the tank and published a Justification for Continued Operation⁴ (JCO) that committed to a video inspection of the tank. This inspection revealed a solid layer floating on the liquid surface. Engineering requested that SRTC assist in obtaining and analyzing samples from this solid layer.

Experimental

Sample collection activities provided three samples of solids from Tank 49H for analysis. Personnel obtained two samples (ITP-542 and ITP-543) using a new sampler designed by the Equipment Engineering Section of SRTC.⁵ The two samples arrived at SRTC in March 1999. An additional sample came from routine operations. Operations personnel saw solids adhering to a plumb bob level indicator and transferred the device to SRTC in April 1999. Researchers split samples ITP-542 and ITP-543, shown in Figure 1, into three sub-samples. Conversely, researchers aggregated the plumb bob samples, shown in Figure 2, and homogenized. They then submitted the ITP-542/3 samples for non-destructive analysis by X-ray diffraction⁶ and organic-constituent analysis by high performance liquid chromatography.⁷ Similarly, they submitted the solids obtained from the plumb bob sample for the same analyses and elemental analysis by inductively coupled plasma-emission spectroscopy.⁸ Additionally, personnel analyzed a sample of the solids by differential scanning calorimetry and thermogravimetric analysis using methods previously described.⁹

Laboratory notebook WSRC-NB-97-62 contains data obtained during these tests and the procedures used. Personnel used routine analytical protocol for the samples discussed in this report.¹⁰

(ITP-543)

(ITP-542)

Figure 1. Initial Samples from Solid Layer in Tank 49H

Results and Discussion

The results of analyses of the solid floating layer of Tank 49H provide key insight for several concerns. First, a discrepancy exists between predicted decomposition rates from the liquid and vapor space sampling. One potential reason for this discrepancy involves the formation of other reaction products such as biphenyl and terphenyl from the tetraphenylborate decomposition. Analysis of these tank solids could substantiate this hypothesis. Secondly, this solid layer could form a barrier for the release of benzene. Similarly, any organic constituents in the solids pose a flammability hazard.

Figure 2. Solids Obtained from Plumb Bob Sample from Tank 49H

ITP-542 and ITP-543

The initial samples obtained from Tank 49H, as shown in Figure 1, contained small pieces colored white and black. Additionally, sample ITP-543 contained a white solid piece. Researchers divided these tank samples (ITP-542 and ITP-543) into 8 sub-samples, segregating the sub-samples by color as white and black. Figures 3 and 4 show the x-ray diffraction patterns obtained from the ITP-543 samples. Examination of the results of the XRD spectra revealed the "white" sample from ITP-543 consisted primarily of sodium carbonate and sodium bicarbonate. The X-ray powder patterns from the black solids and the mixed solids included positive identification of potassium tetraphenylborate, sodium nitrate, sodium aluminosilicate, titanium dioxide and Gibbsite ($\text{Al}(\text{OH})_3$) in addition to sodium carbonate and sodium bicarbonate. The ITP-542 sample contained only a small mass of material insufficient to submit for X-ray diffraction.

Researchers submitted samples of ITP-542 and ITP-543 for analysis of organic components by high performance liquid chromatography. These analyses contact a known mass of sample with a known quantity of acetonitrile. Table 1 lists the measured organic component concentrations (mg/g). The solids contained only minute quantities of organic compounds. As observed in the X-ray pattern, the "white" solids had almost no organic material containing only ~1 mg/g tetraphenylborate and biphenyl. The "black" and "mixed" solids contained higher levels of organic components. However, concentrations, per gram of total solids, ranged from 20 – 40 mg for tetraphenylborate, 40 – 70 mg for biphenyl and 5-55 mg for terphenyl.

Tank 49H Plumb Bob Sample

Waste Pre-Treatment Operations personnel noticed solid adhering to a plumb bob used to measure the tank liquid level. Operations personnel brought the plumb bob, shown in Figure 2, to SRTC for analysis. Researchers ground the solids and submitted them for X-ray diffraction, HPLC, elemental analysis and total organic carbon.

Figure 3. XRD Pattern from ITP-543 Solids "white"

Figure 4. XRD Pattern from ITP-543 Solids "black" and "mixed"

Table 1. HPLC Results* from Tank 49H Solids

Sample	Na(K)TPB	1PB	Biphenyl	Terphenyl
ITP-543-A (Black)	37	6.3	67	5.6
ITP-543-B (White)	1.4	1.1	1.7	0.15
ITP-543-C (Mix)	26	<3	43	2.5
ITP-542-A (Mix)	22	6.2	70	55.1

* Concentration in units of mg/g.

Figure 5 shows the diffraction pattern obtained from the plumb bob sample from Tank 49H. The major components of the sample matrix included sodium nitrate and sodium nitrite. Other components at levels greater than 10 wt % include sodium carbonate and potassium tetraphenylborate. Additionally, X-ray powder pattern indicates the presence of calcium silicate monohydrate.

Researchers submitted a sample of the material obtained from this plumb bob for organic constituents by HPLC analysis. Table 2 contains the results of the organic analysis from the plumb bob sample. As observed in the earlier samples (ITP-542 and ITP-543), the solids do not contain significant quantities of organic compounds. Tetraphenylborate concentrations measured 184 mg/g while biphenyl and terphenyl measured 2.1 mg/L and 4.5 mg/L, respectively. The tetraphenylborate results agree with the X-ray powder pattern data. The level of potassium tetraphenylborate in the plumb bob sample measures about 3 – 4 times higher than the previous samples. The range indicates a significant variability in the solid composition.

Figure 5. X-ray Powder Pattern obtained from Plumb Bob Sample.

Table 2. HPLC Results from Plumb Bob Sample

KTPB	184 mg/g
1PB	3.8 mg/g
Biphenyl	2.1 mg/g
Terphenyl	4.5 mg/g

Table 3 contains the results of the elemental analysis. The sample matrix contains predominantly sodium salts (17.7 wt % on sodium basis) and silica-based compounds (14.7 %) such as calcium or sodium silicate or aluminosilicate. The amount of boron in the sample would equate to approximately 10 wt % of the sample if the boron existed as potassium tetraphenylborate. This agrees well with the HPLC analysis.

Table 3. Elemental Concentrations* from ICP-ES

Al	0.36%
B	0.84%
Ca	0.02%
Cr	0.01%
Cu	0.02%
Ca	0.02%
Fe	0.07%
Mg	0.0003%
Mn	0.004%
Mo	0.001%
Na	17.7%
Ni	0.008%
P	0.037%
Si	14.7%
Sn	0.003%
Ti	0.001%
Zn	0.01%
Zr	0.08%

*Units are weight percent.

The thermal stability of the solid layer in Tank 49H proves important because the layer may represent a potential fuel source if any of the retained benzene ignites. Researchers performed differential scanning calorimetry (DSC) and thermogravimetric

analysis (TGA) on the solids. Figure 6 and Figure 7 contain the DSC and TGA plots for the plumb bob sample, respectively. The DSC scan shows endotherms at 90, 220, 260 and 320 °C. The endotherm at 90 °C reflects evaporation of water and the one at 260 °C may result from the melting of sodium bicarbonate. The DSC scan also exhibits an exotherm at ~ 290-300 °C caused by the decomposition of potassium tetraphenylborate.¹¹ The TGA plot shows weight loss that correlates with the water loss (90 °C) and KTPB decomposition (290-300 °C). Furthermore, the TGA experiment showed no rapid oxidation or combustion at temperatures as high as 800 °C.

Figure 6. The DSC Plot for the Plumb Bob Sample

Figure 7. The TGA Plot for the Plumb Bob Sample

Conclusions

The solid samples obtained from Tank 49H have been analyzed by SRTC. The solids are heterogeneous and consist of inorganic salts and tetraphenylborate salts. Contrary to initial visual observations, the solids do not contain significant quantities of biphenyl and the solid's composition does not help to explain the discrepancy between liquid and

vapor space sample data. The solids exhibit thermal stability at elevated temperature. The only exothermic behavior is the expected decomposition of the minor component, potassium tetraphenylborate.

Acknowledgements

The authors wish to express appreciation to several others whom support this work. These individuals include V. Dukes and J. Mills.

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8 June 99
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