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**Tank 50H Flammability Calculations**

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## Summary

Phase 1 testing is complete. Phase 1 was designed to determine the tetraphenylborate (4PB) decomposition rate of the 4PB present in Tank 50H if Tank 23H or Inhibited Water (IW, water with added sodium nitrite and sodium hydroxide to inhibit corrosion of the carbon steel waste tanks) is added to the tank. Because Phase 2 has several weeks of testing still in progress, the Phase 2 data will be reported in a revision of this report. The following preliminary results, at 95% confidence limits, are presented:

- The 4PB decomposition rate at 50 °C is  $-2.23\text{E-}06 \pm 1.33\text{E-}06$  mol/L/day for Tank 23H and  $-1.74\text{E-}06 \pm 0.35\text{E-}06$  mol/L/day for IW at 50 °C, assuming a linear regression analysis based on the calculated initial 4PB concentrations.
- The maximum benzene generation rate from 4PB decomposition is  $8.90\text{E-}06 \pm 5.30\text{E-}06$  mol/L/day for Tank 23H and  $6.95\text{E-}06 \pm 1.41\text{E-}06$  mol/L/day for IW at 50 °C. This assumes all of the 4PB degrades to benzene.
- Based on our testing, approximately 90% of the 4PB primarily decomposes to phenol, not benzene. The likely benzene generation rate from 4PB decomposition is roughly  $8.90\text{E-}07 \pm 5.30\text{E-}07$  mol/L/day for Tank 23H and  $6.95\text{E-}07 \pm 1.41\text{E-}07$  mol/L/day for IW at 50 °C.
- Because of the limited data available and questions concerning the uniformity of the solids, the 95% confidence limit that gives the most conservative estimate of the 4PB decomposition rate.
- No testing at 100 °C was performed because of the fast decomposition at 50 °C.

The 4PB decomposition is expected to produce primarily phenol, not benzene, during the planned slurring and feeding of the slurry to Saltstone. Pulling a Tank 50H slurry sample towards the end of feeding to Saltstone is recommended. The 4PB analysis of this sample could be used to better estimate the 4PB potential in Tank 50H than a solids estimate combined with analyses of Tank 50H solids after Tank 50H is emptied. This data could be used to formulate a better flammability strategy for Tank 50H.

## Background

Decontaminated liquid waste at the Savannah River Site is grouted for disposal in the Saltstone Facility. Tank 50H serves as a staging tank and routinely transfers supernate to the Saltstone feed tank. During October of 2002, the mass balances for transfers from Tank 50H to Saltstone started to show discrepancies. On October 22, 2002, the differences in mass balance between the two facilities exceeded a preset value of 10 %.

At that time, High Level Waste Operations personnel inserted a video camera into the riser nearest the discharge point to Saltstone and observed a mound of solids. Subsequent to that observation, an inspection in the opposite (northeast) quadrant of the tank revealed a second mound of solids.

In order to remove the solids from Tank 50H, High Level Waste Operations personnel have installed two additional slurry pumps and plan to add either Tank 23H supernate or Inhibited Water to reslurry the solids. Addition of these liquids could increase the decomposition rate of the 4PB and lead to higher benzene generation rate.

SRTC personnel estimated the maximum 4PB decomposition rate to be  $5.0 \text{ mol/day} + 9.6 \times 10^{-7} \text{ mol/L/day}^1$ . Table 1 below summarizes the benzene generation rate at various tank levels.

**Table 1 – Predicted 4PB Decomposition Rate, mol/day**

Volume, gallons	Predicted 4PB decomposition rate, mol/day
<b>300,000</b>	<b>6.1</b>
400,000	6.5
600,000	7.2
800,000	7.9
<b>1,000,000</b>	<b>8.6</b>
1,200,000	9.4
1,400,000	10.1

This task is designed to measure the 4PB decomposition rate for the slurring of the Tank 50H solids with Tank 23H or Inhibited Water solution (Phase 1) and the decomposition rate of any solids left behind after the slurry operation is complete (Phase 2).

### Experimental

Two phases of testing were planned<sup>2</sup> to answer two questions related to two processing decisions.

Phase 1 -- What flammability impact would there be if Tank 23H supernate or inhibited water was used to reslurry the Tank 50H solids? Would the addition lead to high benzene generation rates?

Phase 2 -- If some Tank 50H solids were left behind after attempting to reslurry the Tank 50H solids, what flammability impact would there be if a high hydroxide or high nitrate (low hydroxide) supernate was transferred into Tank 50H? Would the addition lead to high benzene generation rates?

Actual Tank 50H solids were used in each of the experiments. A solution (Tank 23 waste, IW, high hydroxide or low hydroxide simulant) was combined with the Tank 50H solids in a 250 ml polypropylene sample bottle. The bottles were temperature controlled and mixed by placing them in an orbital shaker to simulate the expected Tank 50H temperature (ambient and 50 °C). After the slurry was held at temperature for the desired hold time (one to six weeks), the sample bottle was removed from the orbital shaker and submitted to ADS for analysis. Tom White of ADS extracted the organic from the sample using acetonitrile and analyzed the extracted sample for 4PB degradation

products using High Pressure Liquid Chromatography (HPLC). Knowing the extraction efficiency of the solvent, the 4PB degradation products can be accurately estimated. The concentration of 4PB in the analysis was used to estimate the 4PB degradation rate. The degradation products were used to determine the extent of the degradation and as a secondary method for calculating the degradation rate.

### Solids Preparation

Early testing showed that 4PB analyses varied from 60-1150 mg 4PB/L solids<sup>3</sup>. The tank 50H solids were not uniform in composition, so care was taken to homogenize the Tank 50H solids. The solids were placed in a dish and the solid size was reduced using a pestle and scoopula. The homogenized solids were added to a 500 ml wide mouth polyethylene bottle and were then split into 1.8 g sub-samples.

### Sample Preparation

Even after the solids were homogenized, 4PB variability within the sub-samples was similar to the variability of the original Tank 50H solids samples. In order to minimize the impact of sample variability, a decision was made to extract the organic from the whole sample rather than trying to pull a representative sub-sample from the bottle. In order to treat the 1.8 g solid sample, the entire sample was contacted with acetonitrile to extract the organic species. Analysis of the samples by this method led to minimal sample to sample variation (Table 2). In order to demonstrate that acetonitrile was a reliable method for extracting the organic species of interest, a second extraction with the same sample and no 4PB or degradation products were detected.

Based on these analyses, using 95% confidence limits, the Tank 50H solids contain  $357.7 \pm 8.0$  mg 4PB/kg solids, <20 3PB mg/kg solids, <20 mg 2PB /kg solids, <20 mg 1PB /kg solids and  $41.0 \pm 5.0$  mg phenol /kg solids.

**Table 2 – 4PB analysis of 1.8 gram sub-samples, mg/kg solids**

<u>Sample ID</u>	<u>4PB</u>	<u>3PB</u>	<u>2PB</u>	<u>PBA</u>	<u>Phenol</u>
3-192053	354	<20	<20	<20	39
3-192054	359	<20	<20	<20	43
3-192055	360	<20	<20	<20	41

Based on the above Solids composition and the mass of the added solutions, the starting concentration of 4PB and degradation products was calculated for the various solutions. The results are reported in Table 3.

**Table 3 – Predicted Starting Composition, mg/kg**

Added Solution	Solution Density, g/ml	Added Solution, ml	Added Solution Mass, g	Solids mass, g	Solution mass, g	Concentration, mg/kg				
						4PB	3PB	2PB	PBA	Phenol
Tank 23	1.005	17	17.085	1.8	18.885	34.1	<2	<2	<2	3.9
Inhibited water	1	17	17	1.8	18.8	34.2	<2	<2	<2	3.9
Inhibited water	1	5.2	5.2	1.8	7	92.0	<2	<2	<2	10.5
High Hydroxide	1.244	17	21.148	1.8	22.948	28.1	<2	<2	<2	3.2
High Nitrate	1.271	17	21.607	1.8	23.407	27.5	<2	<2	<2	3.2

**Phase 1 – Slurry Testing**

Phase 1 testing was designed to measure the tetraphenyl borate decomposition rate and benzene generation rate if the Tank 50H solids were combined with Tank 23H supernate or Inhibited Water (IW, 0.01 M sodium nitrite, 0.01 M sodium hydroxide). HLW personnel will use either Tank 23H supernate or IW to attempt to reslurry the Tank 50H solids. Because a limited quantity of Tank 23H supernate was available, most of the Phase 1 testing was completed with IW. The Phase 1 experiments are summarized in Table 4.

**Table 4 -- Phase 1 Experiment Summary Table**

Experiment	Temp, °C	Solution	# Weeks	Solids Required, g	Liquid Required, mL
Task1 Experiment 1	50 °C	Inhibited Water	6	1.8	5.1
Task1 Experiment 2	Ambient	Inhibited Water	2	1.8	17
Task1 Experiment 3	50 °C	Tank 23H	6	1.8	17
Task1 Experiment 4	50 °C	Inhibited Water	6	1.8	17

The Tank 50H solids were combined with liquid in a 250 ml polypropylene sample bottle. The samples were capped, placed in a room temperature or 50 °C orbital shaker, and held at temperature as long as required. The sample bottle was removed and submitted to ADS for analyses. ADS consumed the entire sample by using acetonitrile to extract the organic from the sample. The Tank 50H samples were 357.7 mg 4PB/kg solids which would give a starting concentration of ~30 mg 4PB/kg slurry after combining the Tank 50H solids with 17 ml of solution or ~90 mg 4PB/kg slurry after combining the Tank 50H solids with 5.1 ml of solution.



**Figure 1 – Photograph of Tank 50H solids plus Inhibited Water**

**Phase 2 – Solids Left Behind Testing**

If the Tank 50H solids could not be removed by slurring and pumping them to Saltstone, would there be any disadvantage to leaving the solids in Tank 50H and allowing any HLW to be transferred into Tank 50H? The Phase 2 experiments are summarized in Table 5.

**Table 5 - Phase 2 Experiments Summary Table**

<b>Experiment</b>	<b>Temp, °C</b>	<b>Solution</b>	<b># Weeks</b>	<b>Solids Required, g</b>	<b>Liquid Required, mL</b>
Task2 Experiment 1	Ambient	High Hydroxide Simulant	6	1.8	17
Task2 Experiment 2	50 °C	High Hydroxide Simulant	6	1.8	17
Task2 Experiment 3	Ambient	Low Hydroxide Simulant	6	1.8	17

Two solutions were chosen to represent the extremes, a high hydroxide simulant and a high nitrate (low hydroxide) simulant. These simulants have been used in a variety of SRS and ORNL tests since 1991.<sup>4</sup> A suite of catalysts, sludge, and MST (Enhanced Catalyst Composition<sup>5</sup> or ECC) was added to ensure that any metal catalyst that might

decompose the 4PB would be present in the simulant. The simulants (Table 6) and ECCs (Table 7) are summarized below.

**Table 6 – Recipe for High Hydroxide and High Nitrate Simulants**

Target Na <sup>+</sup> (M)			5.6		5.6	
Volume required (L):			1.00		1.00	
Simulant			High Hydroxide Simulant		High Nitrate Simulant	
Component	Form	MW	Molarity	Required (g)	Molarity	Required (g)
NaOH	NaOH	40	3.05	165.52	1.17	98.40
NaNO <sub>3</sub>	NaNO <sub>3</sub>	84.99	1.08	20.40	2.84	159.43
NaNO <sub>2</sub>	NaNO <sub>2</sub>	69	0.740	51.06	0.370	25.53
NaAlO <sub>2</sub>	Al(NO <sub>3</sub> ) <sub>3</sub> •9H <sub>2</sub> O	375.14	0.270	101.29	0.320	120.04
Na <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	142.04	0.0300	4.26	0.220	31.25
Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O	124.01	0.170	21.08	0.160	19.84
NaCl	NaCl	58.44	0.0100	0.563	0.0400	2.329
NaF	NaF	41.99	0.0100	0.420	0.0500	2.100
Na <sub>3</sub> PO <sub>4</sub>	Na <sub>3</sub> PO <sub>4</sub> •12H <sub>2</sub> O	380.13	0	0.000	0	0.000
Na <sub>2</sub> HPO <sub>4</sub>	Na <sub>2</sub> HPO <sub>4</sub> •7H <sub>2</sub> O	268.09	0.0080	2.145	0.0100	2.681
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	134	0.0080	1.072	0.0080	1.072
Na <sub>2</sub> SiO <sub>3</sub>	Na <sub>2</sub> SiO <sub>3</sub> •9H <sub>2</sub> O	284.2	0.00400	1.137	0.00400	1.137
Na <sub>2</sub> MoO <sub>4</sub>	Na <sub>2</sub> MoO <sub>4</sub> •2H <sub>2</sub> O	241.95	0.0002	0.0484	0.0002	0.0484
KNO <sub>3</sub>	KNO <sub>3</sub>	101.1	0.0300	3.0330	0.00410	0.4145
CsCl	CsCl	168.36	0.00037	0.0623	0.00014	0.0236
Water	Water	18.018		871.8		806.3

**Table 7 – Enhanced Catalyst Composition**

Component	Compound	Species Concentration in Slurry (mg/L)
Pd	Pd(NO <sub>3</sub> ) <sub>2</sub>	13.0
Cu	Cu(SO <sub>4</sub> •5H <sub>2</sub> O)	3.7
Hg	Hg(NO <sub>3</sub> ) <sub>2</sub> •H <sub>2</sub> O	2.2
diphenylmercury	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Hg	150
Mo/Cr/Si/Se/As	Na <sub>2</sub> MoO <sub>4</sub> •2H <sub>2</sub> O	12
	Na <sub>2</sub> CrO <sub>4</sub>	60
	Na <sub>2</sub> SiO <sub>3</sub> •9H <sub>2</sub> O	16
	Na <sub>2</sub> SeO <sub>4</sub>	1
	As <sub>2</sub> O <sub>3</sub>	0.04
Zn/Pb/Fe	Zn(NO <sub>3</sub> ) <sub>2</sub> •4H <sub>2</sub> O	8.8
	Pb(NO <sub>3</sub> ) <sub>2</sub>	1.2
	Fe(NO <sub>3</sub> ) <sub>3</sub> •9H <sub>2</sub> O	2.6
Sn	SnCl <sub>2</sub>	2.1
Ca/La/Co	Ca(NO <sub>3</sub> ) <sub>2</sub> •4H <sub>2</sub> O	12.2
	La(NO <sub>3</sub> ) <sub>3</sub> •6H <sub>2</sub> O Co(NO <sub>3</sub> ) <sub>2</sub> •6H <sub>2</sub> O	0.05 0.04
Cd/Ce	Cd(NO <sub>3</sub> ) <sub>2</sub> •4H <sub>2</sub> O	0.4
	Ce(NO <sub>3</sub> ) <sub>3</sub> •6H <sub>2</sub> O	0.3
Rh	Rh(NO <sub>3</sub> ) <sub>3</sub>	1.4
Ag	AgNO <sub>3</sub>	6.8
Ru	RuCl <sub>3</sub> •xH <sub>2</sub> O	5.4
sludge*	Sludge	500
MST&	MST	500

\* SRTC Purex simulant sludge (IDMS last batch of Purex 01-16-97 without noble metals).

& Monosodium titanate from TNX containing 1 wt % composite of three 1 Liter bottles dated 01-23-01. Mark Barnes previously used this material for other testing<sup>6</sup>.

Testing was completed as was described in Phase 1. For each test, six sample bottles were prepared by combining 1.8 g Tank 50H solids, and 17 ml simulant with noble metals. The sample bottles were placed in a shaker bath and pulled as required for analysis.

## Results

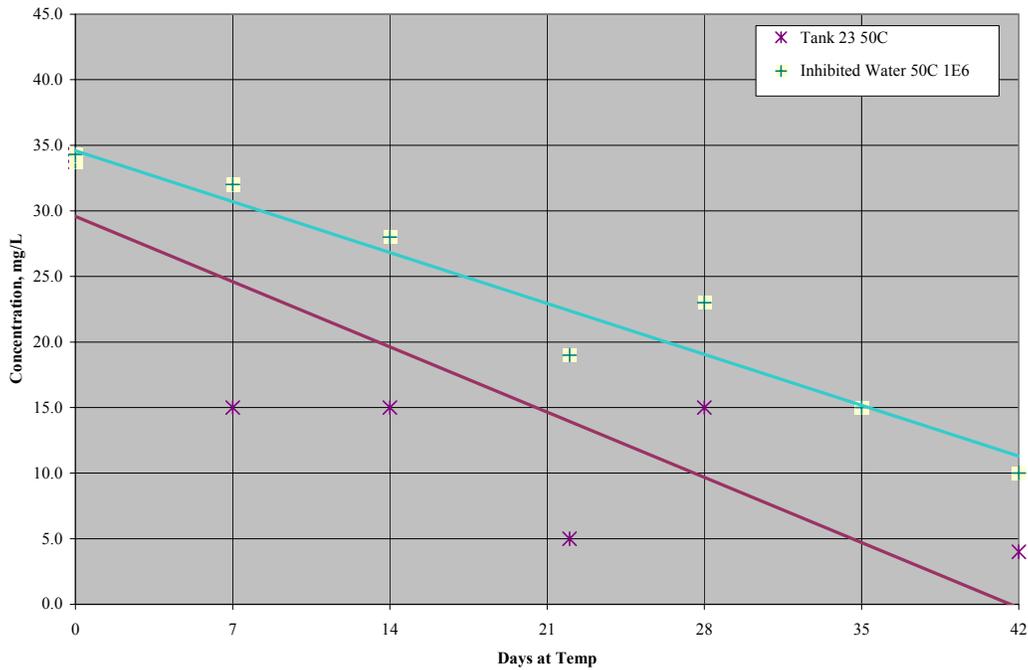
### Phase 1 – Slurry Testing

#### Question 1 – What is the 4PB decomposition rate of Tank 50H solids in Tank 23H and Inhibited Water?

Experiments 3 and 4 were designed to be identical; except that experiment 3 used Tank 23H supernate and experiment 4 used IW. The data are summarized in Figure 2\*. As can be seen from the data, Tank 23H leads to faster 4PB decomposition than Inhibited Water. Based on this data, the 4PB decomposition rate is  $-2.23\text{E}-06 \pm 1.33\text{E}-06$  mol/L/day for Tank 23H and  $-1.74\text{E}-06 \pm 0.35\text{E}-06$  mol/L/day for IW at 50 °C, assuming a linear

\* 0.3 E6 in the Figure 2 refers to experiments simulating the addition of 300,000 gallons of liquid. 1.0 E6 refers to experiments simulating the addition of 1,000,000 gallons of liquid.

regression analysis based on the calculated initial 4PB concentrations. Note at these rates, the 4PB would be destroyed in six to nine weeks.



**Figure 2 – 4PB Degradation Rate Comparison of IW versus Tank 23H supernate**

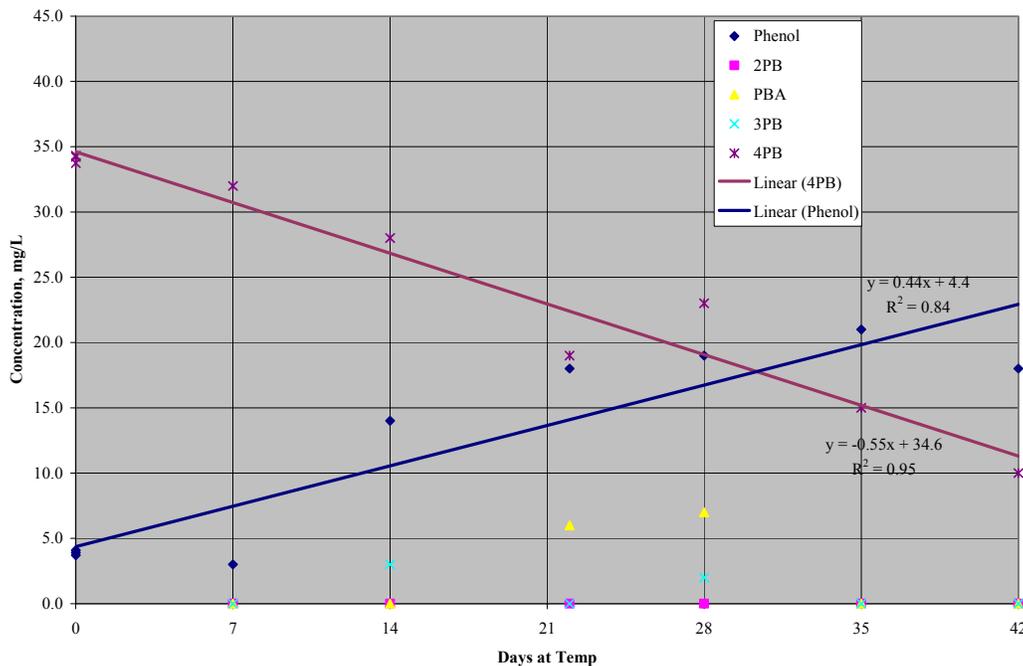
**Question 2 – What is the benzene generation rate of Tank 23H compared to IW?**

The maximum benzene generation rate is four times the 4PB decomposition rate or  $8.90E-06 \pm 5.30E-06$  mol/L/day for Tank 23H and  $6.95E-06 \pm 1.41E-06$  mol/L/day for IW at 50 °C, assuming a linear regression analysis based on the calculated initial 4PB concentrations. 4PB can decompose to a variety of products including benzene and phenol. Although the 4PB decomposition rate is fast in the experiments at 50 °C, the phenol concentration suggests that the predominant decomposition product is phenol, not benzene. Samples taken at the end of the third week of testing were analyzed for both benzene and phenol using GC/MS. Note there is 10-15 times as much phenol as benzene in these samples. The data from the first three weeks is summarized in Table 8. Based on this data, the benzene generation rate is  $8.90E-07 \pm 5.30E-07$  mol/L/day for Tank 23H and  $6.95E-07 \pm 1.41E-07$  mol/L/day for IW at 50 °C.

**Table 8 – Data Comparison for Week #3 Testing comparing IW and Tank 23H at 50 °C**

Experiment / Analyte →	HPLC, mg/L					SVOA, mg/L	
	4PB	3PB	2PB	PBA	Phenol	Phenol	Benzene
Tank 50	5	<1	<1	6	26	24	2.5
Inhibited Water	19	<1	<1	6	18	27	1.8

Note also that the destruction rate of 4PB is nearly equal to the phenol generation rate, suggesting that the primary decomposition product is phenol, not benzene. The data is summarized in Figure 3.



**Figure 3 – Phenol and 4PB concentration profiles for IW plus Tank 50H solids at 50 °C**

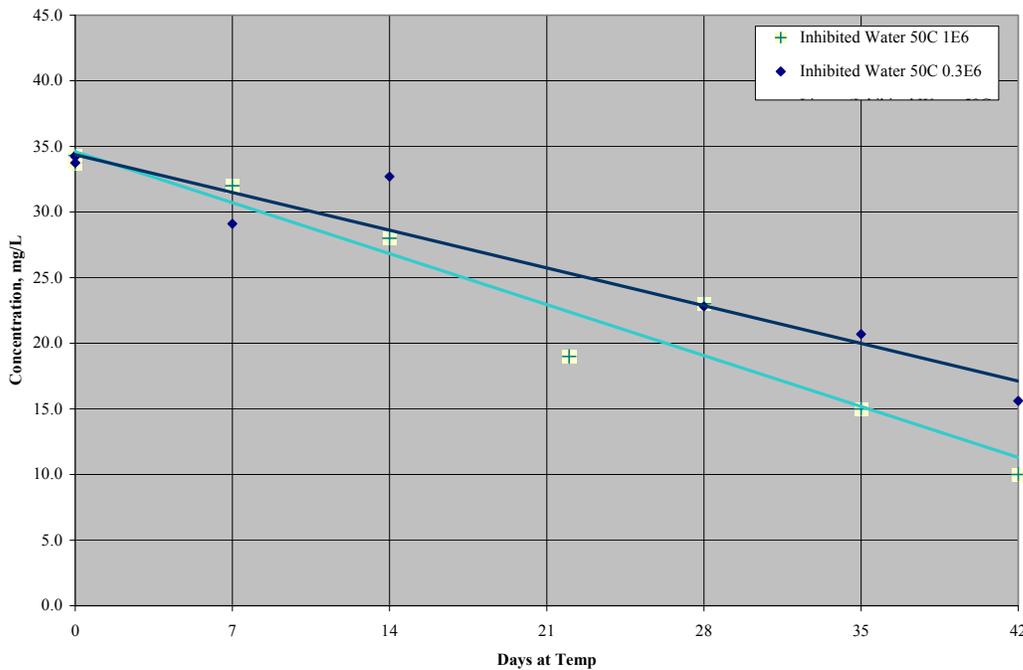
**Question 3 – What is the 4PB decomposition rate with 300,000 gallons of IW versus 1,000,000 gallons of IW?**

Experiments 1 and 4 were designed to be identical; except that experiment 2 added 5.1 ml of inhibited water to 1.8 g Tank 50H solids to simulate the addition of 300,000 gallons of IW to Tank 50H. Experiment 2 added 17 ml of inhibited water to 1.8 g Tank 50H solids to simulate the addition of 1,000,000 gallons of IW to Tank 50H. Both experiments were performed at 50 °C.

To simplify the comparison of the two experiments, the data at 300,000 gallons were corrected by dilution as if 1,000,000 gallons were present. The data is summarized in Table 9. The 4PB decomposition rate is  $-4.87 \pm 1.33$  mol/day at 300,000 gallons and  $-6.58 \pm 1.33$  mol/day at 1,000,000 gallons. The higher decomposition rate at the higher volume is likely due to (1) faster dissolution of the Tank 50H solids since more solution is present and (2) the Tank 23H solution likely contains catalysts that increase the 4PB decomposition and more solution would add more catalyst to the solids. The decomposition rate is 34% higher at the higher volume.

**Table 9 – Comparison of decomposition rate of 300,000 gal versus 1,000,000 gal**

	<u>Time, days</u>	<u>4PB</u>	<u>3PB</u>	<u>2PB</u>	<u>1PB</u>	<u>Phenol</u>
Inhibited Water 50 °C 300,000 gallons corrected	7	29.1	0.90	-	-	0.9
	14	32.7	1.50	1.50	2.10	9.9
	28	22.8	1.50	-	3.00	14.7
	35	20.7	1.50	-	2.10	15.9
	42	15.6	1.50	-	-	16.5
Inhibited Water 50 °C 1,000,000 gallons	7	32	<1	<1	<2	3
	14	28	3	<1	<2	14
	22	19	<1	<1	6	18
	28	23	2	<5	7	19
	35	15	<1	<1	<5	21
	42	10	<2	<2	<2	18



**Figure 4 – Comparison of Decomposition Rate at Low versus High Tank Volume**

#### **Question 4 – What is the 4PB decomposition rate at 25 °C compared to 50 °C?**

Experiments 2 and 4 were designed to be identical; except that experiment 2 used IW at 25 °C and experiment 4 used IW at 50 °C. Based on the limited information, there is no way to predict this from the data we collected (we only have two weeks of data at 25 °C and one of the two 4PB values is 60 mg/L, much higher than the starting concentration). This question will be answered with Phase 2 data.

#### **Phase 2 – Solids Left Behind Testing**

The results of Phase 2 will be documented in a later revision of this report.

#### Conclusions

The 4PB in the Tank 50H solids decomposed rapidly during testing with Tank 23H and Inhibited Water solutions at 50 °C. It is expected that the 4PB will decompose rapidly in Tank 50H if the liquid temperature approaches 50 °C during the planned operation to slurry the Tank 50H solids and feed the resultant solution to Saltstone. During these evolutions, most of the 4PB is expected to decompose. The following are the conclusions from this testing.

- The 4PB decomposition rate at 50 °C is  $-2.23\text{E-}06 \pm 1.33\text{E-}06$  mol/L/day for Tank 23H and  $-1.74\text{E-}06 \pm 0.35\text{E-}06$  mol/L/day for IW at 50 °C, assuming a linear regression analysis based on the calculated initial 4PB concentrations.
- The maximum benzene generation rate from 4PB decomposition is  $8.90\text{E-}06 \pm 5.30\text{E-}06$  mol/L/day for Tank 23H and  $6.95\text{E-}06 \pm 1.41\text{E-}06$  mol/L/day for IW at 50 °C. This assumes all of the 4PB degrades to benzene.
- Based on our testing, approximately 90% of the 4PB primarily decomposes to phenol, not benzene. The likely benzene generation rate from 4PB decomposition is roughly  $8.90\text{E-}07 \pm 5.30\text{E-}07$  mol/L/day for Tank 23H and  $6.95\text{E-}07 \pm 1.41\text{E-}07$  mol/L/day for IW at 50 °C.
- Because of the limited data available and questions concerning the uniformity of the solids, the 95% confidence limit that gives the most conservative estimate of the 4PB decomposition rate.
- No testing at 100 °C was performed because of the fast decomposition at 50 °C.

The 4PB decomposition is expected to produce primarily phenol, not benzene, during the planned slurring and feeding of the slurry to Saltstone. Pulling a Tank 50H slurry sample towards the end of feeding to Saltstone is recommended. The 4PB analysis of this sample could be used to better estimate the 4PB potential in Tank 50H than a solids estimate combined with analyses of Tank 50H solids after Tank 50H is emptied. This data could be used to formulate a better flammability strategy for Tank 50H.

#### Acknowledgements

The authors wish to thank Bill Wilmarth, Sam Fink and Tom Peters for their suggestions for designing the experiments and to Bill Wilmarth for supplying the Tank 50H solids.

Also, thanks to Chris Martino for his perseverance in initiating testing to measure the 4PB decomposition rate and to Rob Swingle for providing information concerning the composition of the Tank 23H solution.

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