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Benzene Generation Testing for Tank 48H Waste Disposition

T. B. Peters
M. J. Barnes
S. D. Fink

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Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808



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LIST OF ACRONYMS

3PB	triphenylborane
2PB	diphenylborinic acid
1PB	phenylboronic acid
ADS	Analytical Development Section
B	boron
Cs	cesium
CsTPB	cesium tetraphenylborate
DWPF	Defense Waste Processing Facility
HLW	High Level Waste
HPLC	High Performance Liquid Chromatography
ICP-ES	Inductively Coupled Plasma – Emissions Spectroscopy
K	potassium
KTPB	potassium tetraphenylborate
SRS	Savannah River Site
SRNL	Savannah River National Laboratory
SPF	Saltstone Production Facility
TPB	tetraphenylborate
WPTS	Waste Processing Technology Section

1.0 EXECUTIVE SUMMARY

In support for the Aggregation option¹, researchers performed a series of tests using actual Tank 48H slurries. The tests were designed to examine potential benzene generation issues if the Tank 48H slurry is disposed to Saltstone. Personnel used the archived Tank 48H sample (HTF-E-03-127, collected September 17, 2003) for the experiments. The tests included a series of three experiments (Tests A, B, and F) performed in duplicate, giving a total of six experiments. Test A used Tank 48H slurry mixed with ~20:1 with Defense Waste Processing Facility (DWPF) Recycle from Tanks 21H and 22H. Test B used Tank 48H slurry mixed with ~ 2.7:1 with DWPF Recycle from Tanks 21H and 22H, while Test F used Tank 48H slurry as-is. Tests A and B occurred at 45 °C, while Test F occurred at 55 °C.

Over a period of 8 weeks, personnel collected samples for analysis, once per week. Each sample was tested with the in-cell gamma counter. The researchers noted a decline in the cesium activity in solution which is attributed to temperature dependence of the complex slurry equilibrium. Selected samples were sent to ADS for potassium, boron, and cesium analysis. The benzene generation rate was inferred from the TPB destruction which is indirectly measured by the in-growth of cesium, potassium or boron. The results of all the analyses reveal no discernible in-growth of radiocesium, potassium or boron, indicating no significant tetraphenylborate (TPB) decomposition in any of the experiments. From boron measurements, the inferred rate of TPB destruction remained less than 0.325 mg/(L-h) implying a maximum benzene generation rate of <0.332 mg/(L-h).

2.0 INTRODUCTION

Tank 48H currently contains approximately 250,000 gallons of alkaline slurry with potassium and cesium tetraphenylborate (KTPB and CsTPB) from the operation of the In-Tank Precipitation process. This material is not compatible with the waste treatment facilities at Savannah River Site (SRS) and must be removed or undergo treatment to destroy the organic compounds before Tank 48H can be returned to Tank Farm service. Return of the tank to routine service is an essential element for operation of the overall system.

Aggregation is one remediation option for the Tank 48H material.¹ However, personnel identified a technology gap, or risk, in the adequacy of understanding the generation rate for benzene during this proposed option.² To mitigate this risk, Salt Engineering authorized ("Benzene Generation Testing for Tank 48H Disposition," SP-TTR-2004-00003) this experimental study using actual waste samples to provide measurements of tetraphenylborate (TPB) decomposition rates and the implied benzene generation rates.³ SRNL researchers wrote a task plan encompassing the scope of work.⁴ This report

details the results of the completed experiments to measure benzene generation rates for this processing option.

3.0 EXPERIMENTAL

Personnel used the archived Tank 48H sample (HTF-E-03-127, collected September 17, 2003) for the experiments.⁵ Since collection of the sample, Operations added caustic solution to bring the free hydroxide content of the waste above 1 M. Accordingly, the technicians adjusted the waste slurry used for these tests to approximate the current Tank 48H conditions. The adjustment via the addition of 50 wt % caustic caused an effective 2.7% volume increase of the slurry.

After this initial caustic addition, the Tank 48H slurry was prepared according to the needs of each experiment. The added waste used was primarily from DWPF recycle.^a As the future composition of the recycle is not known, a composite of samples from Tanks 21H and 22H supernate – which consists primarily of DWPF Recycle material – was used. For Tests A-1 and A-2, personnel mixed 7.5 mL of the Tank 48H slurry with 143 mL of DWPF recycle. In Tests B-1 and B-2, technicians added 55 mL of Tank 48H slurry with 95 mL of DWPF recycle. Tests F-1 and F-2 used 150 mL of the Tank 48H slurry with no other additives. For each of the experiments, a filtrate sample (i.e., well mixed slurry was filtered through a 0.45 μ m syringe filter) was pulled after preparing the slurry, and before the bottles were placed in their respective water baths. This sample serves as the time = 0 data point. Table 1 lists the experimental conditions for each of the experiments.

Table 1. List of Experiments and Generic Conditions.

Test ID	TPB Concentration#	pH	Temperature
A	1,000 mg/L	~12.5	45 °C
B	7,500 mg/L	~13.5	45 °C
F	20,600 mg/L	~14	55 °C

[#] The three concentrations represent specific ratios of Tank 48H waste with DWPF Recycle Stream waste: 20,600 mg/L TPB - Tank 48H waste as-is, at full (current) TPB concentration, 7500 mg/L TPB – maximum bounding concentration for aggregation strategy, and 1000 mg/L TPB – minimum reasonable bounding concentration for the aggregation strategy.

During the time of the experiments, the water baths were heated to a constant temperature (± 3 °C) with the experiments constantly agitated using a magnetic stirrer.

^a The DWPF recycle was approximately by volume 50% Tank 21H samples (HTF-571, -572, -573, and -574) and 50% Tank 22H samples (HTF-575, -576, -577, and -578). The samples were received July 2, 2003.

The experiments monitored the decomposition of the organic (KTPB/CsTPB) at elevated temperature over an 8 week period. Sample collection occurred weekly (i.e., 9 total samples per vessel, including the time = 0 sample). Personnel collected filtrate samples, using 0.45 micron or smaller pore size media, for chemical analyses. Chemical analyses included determination of ^{137}Cs concentration – as a measure of decomposition of the CsTPB – using the gamma counter available within the Cells. Selected samples also received potassium analysis by the Analytical Development Section outside the Cells using Inductively Coupled Plasma – Emissions Spectroscopy (ICP-ES). The task plan indicated that personnel would analyze a final slurry sample from the vessels using High Performance Liquid Chromatography (HPLC) to determine the net destruction of TPB during the 8 week period. However, the gamma counts and ICP-ES analyses showed no indication of any reaction, so the HPLC analyses were not performed. The results were recorded into the experimental notebook.⁶

4.0 EXPERIMENTAL RESULTS

4.1 Gamma Count Results

For the six experiments, a total of 9 filtrate samples were pulled for gamma counting. The in-cell gamma counter was used to measure gamma activity. The data is presented in Table 2, while Figure 1 is a graphical display of the data.

Table 2. Gamma Count Results

Time (days)	Cesium-137 Activity (dpm/mL)					
	A-1	A-2	B-1	B-2	F-1	F-2
0 (predicted)	3.03E+06	3.03E+06	1.10E+07	1.10E+07	2.69E+07	2.69E+07
0	8.37E+06	1.43E+07	1.94E+07	1.96E+07	5.26E+07	4.73E+07
7	2.70E+06	3.55E+06	1.19E+07	1.24E+07	3.10E+07	3.37E+07
14	3.13E+06	3.00E+06	1.08E+07	1.06E+07	2.80E+07	2.87E+07
21	2.65E+06	2.21E+06	2.99E+06	2.93E+06	2.60E+07	2.53E+07
28	NA	NA	9.67E+06	6.35E+06	1.78E+07	2.26E+07
35	2.52E+06	2.22E+06	9.98E+06	1.07E+07	2.37E+07	2.62E+07
42	1.95E+06	1.88E+06	8.92E+06	8.79E+06	2.39E+07	2.41E+07
49	2.24E+06	2.06E+06	9.10E+06	8.45E+06	2.37E+07	2.34E+07
56	1.87E+06	1.58E+06	8.98E+06	8.66E+06	2.26E+07	2.35E+07

NA = not available as the background was greater than the sample activity

The initial filtrate activities are higher than predicted. This increased filtrate activity occurs in each of the six experiments. The authors eliminated experimental and

procedural error as a potential reason for this difference and consider the temporary increase to be from an actual physical phenomenon.

Any decomposition of CsTPB would increase the quantity of ^{137}Cs in solution and thus increase the filtrate activity. In each of the experiments, the researchers noted a decline in ^{137}Cs activity over time. The decrease in activity does not indicate the formation of TPB. At time = 35 days, the ^{137}Cs activity in each experiment stabilized at approximately the predicted activity (Figure 1). In Figure 1, the short dashed lines indicate the predicted filtrate cesium activity for each experiment. The decline in cesium activity for the experiments is likely caused by the temperature dependence of the complex equilibrium from dissolution of potassium and cesium tetrphenylborate during heating (i.e., the initial data point was taken at $\sim 20^\circ\text{C}$). Due to the differing solubility and relative masses of both species, when the slurries warm to reaction temperature, the increase in TPB concentration from KTPB dissolution (i.e., more soluble than CsTPB) in solution promotes precipitation of CsTPB, thus lowering the amount of cesium in solution.⁷

Between the initial high cesium results and the decline in filtrate activity, a concern exists that the decline in activity may mask – or hide – some TPB destruction. However, the boron data corroborates the cesium data in that both measurements indicate no detectable TPB destruction. Although the potassium data has larger uncertainty during periods of the experiment, the measured values also corroborate the cesium data implying negligible TPB destruction. As all three analytical methods give the same conclusion, the composite dataset indicates that there is no TPB destruction that is being masked by the decline in cesium activity.

From the portion of the gammascan data that had stabilized (35 to 56 days), the researchers calculated the minimum detectable rate for the average of each test (A, B, F). At the end of 56 days, the minimum detectable rate for each experiment exceeded the difference between any of the data points, even accounting for the analytical uncertainty. The gamma count results for all experiments indicate negligible decomposition of CsTPB occurred.

From the portion of the gammascan data that had stabilized (35 to 56 days), SRNL calculated the rates of reaction. As a comparison, researchers calculated the minimum detectable decomposition rate for the average of each test. The minimum detectable rate represents the rate below which decomposition cannot be distinguished from analytical noise. The minimum detectable decomposition rate is determined for each experiment by taking the starting data point, and increasing the % destruction value by the 2σ analytical uncertainty (1.93 %).^b This new value is then assigned to a new point at the end of the experiment (56 days). For example, for the average of experiment A-1 and A-2, the time

^b The uncertainty was calculated from the deviation of the standards over time and was calculated to be 1.93%.

= 0 data point is $2.32\text{E}+06$ dpm/mL. The new data point is assigned an activity of $2.36\text{E}+06$ dpm/mL ($2.32\text{E}+06 \times 1.0193$). Experiments A-1 and A-2 ran for 504 hours (21 days \times 24 hours/day), so the new data point is set to time = 504 hours. From the starting time (35 days) data point and the new data point (56 days), a line is drawn. This line represents the minimum detectable rate over the time of the experiment. The minimum detectable rate is determined for the average of each pair of experiments; A, B, and F. The minimum detectable rate is then compared to the data points that determine the rate. In the case of our experiments, all the data points of A, B, and F lie beneath the line representing the minimum detectable rate (Table 3). Therefore, we can determine that if any TPB decomposition is occurring, it is at a level beneath what we can detect.

Table 3. Reaction Rates as a Function of Gamma Scan Data

Experiment	Benzene Generation Rate (mg/(L-hour))	TPB Destruction Rate (mg/(L-hour))
Average A	<7.95E-03	<8.11E-03
Average B	<3.52E-02	<3.59E-02
Average F	<8.55E-02	<8.72E-02

4.2 ICP-ES Results for Potassium and Boron

Researchers analyzed selected samples via ICP-ES. For each experiment, we analyzed the Day 0, 6, and 85 samples. While the gamma scan analyses stopped at 56 days, we pulled samples at day 85 for ICPES analyses. We also examined the Day 28 samples for experiments F-1 and F-2. The task plan specified analysis of final ICP-ES samples, which are the time 85 samples. Table 4 contains the tabular data and Figures 2 and 3 contain the graph of those data points.

The large variances in the potassium data ^c make a detailed conclusion difficult; however, a lack of potassium in-growth is apparent. This indicates a lack of KTPB decomposition during the reactions.

The boron data presents a much clearer perspective (Figure 3). With a low uncertainty in each data point (5%), the lack of any in-growth indicates a lack of any reaction. In the figure, the data points in experiment A-2 are obscured by the A-1 data points.

The Minimum detectable rate was determined from boron data in the same fashion as with the gamma scan data. The starting point is the Day 6 sample, and the end is the Day 85 sample. The time 0 data point is omitted from the plot as the increase in boron across 5 of 6 experiments looks to be a function of increased solubility due to the solution

^c Most of the potassium data points were either below detection limits or close to it.

temperature increase at that time.^d The resulting line shows greater slopes than the comparable experimental data. Test F-1 has a final data point that could surpass the minimal detectable rate if adding the uncertainty. However, the average of the two F data points still is less than the minimal detection limit. Therefore, we can determine that if any TPB decomposition is occurring, it is at a level beneath what we can detect.

Table 4. Potassium and Boron Results

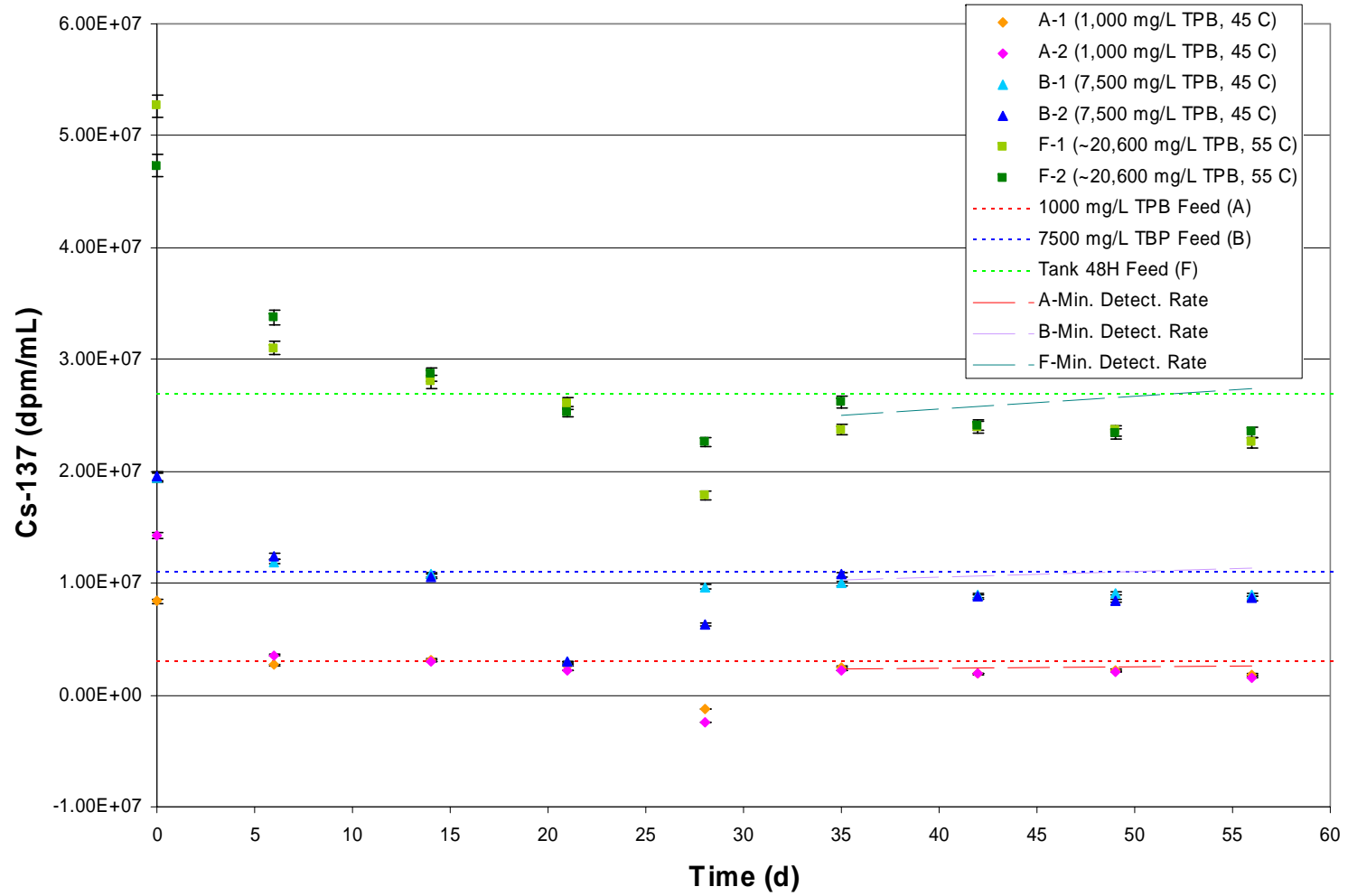
Sample ID	Time (days)	Potassium (mg/L)	Uncertainty (mg/L)	Boron (mg/L)	Uncertainty (mg/L)
A-1	0	52.7	35.3	26.1	1.31
	6	< 167	NA	33.9	1.69
	85	27.8	5.56	29.5	1.48
A-2	0	35.1	37.2	25.7	1.29
	6	< 177	NA	34.6	1.73
	85	30.9	6.18	31.0	1.55
B-1	0	199	43.7	173	8.67
	6	209	328	188	9.39
	85	96.1	19.2	132	6.60
B-2	0	193	44.4	184	9.21
	6	< 168	NA	182	9.10
	85	99.7	19.9	165	8.25
F-1	0	283	289	425	21.2
	6	219	343	432	21.6
	28	296	237	424	21.2
	85	264	52.8	430	21.5
F-2	0	336	138	407	20.4
	6	269	323	420	21.0
	28	251	244	418	20.9
	85	267	53.4	413	20.7

^d The time=0 sample was taken at room temperature, before the water bath had heated to temperature.

Table 5. Reaction Rates as a Function of Boron Data

Experiment	Benzene Generation Rate (mg/(L-hour))	TPB Destruction Rate (mg/(L-hour))
Average A	<2.61E-02	<2.66E-02
Average B	<1.41E-01	<1.44E-01
Average F	<3.25E-01	<3.32E-01

Figure 1. Graph of Gamma Scan Data



Time=0 data point is at room temperature.

Figure 2. Graph of Potassium Data

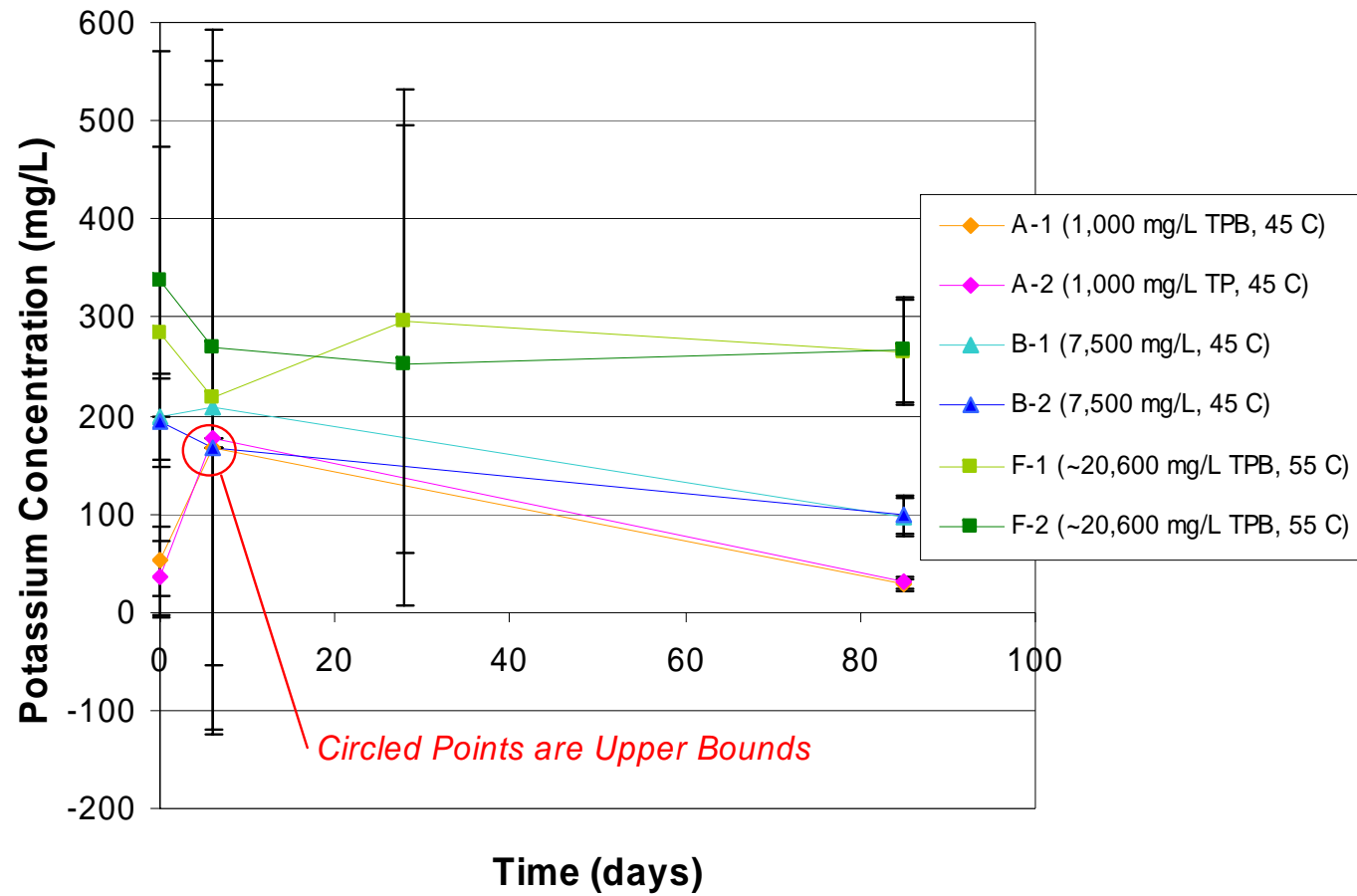
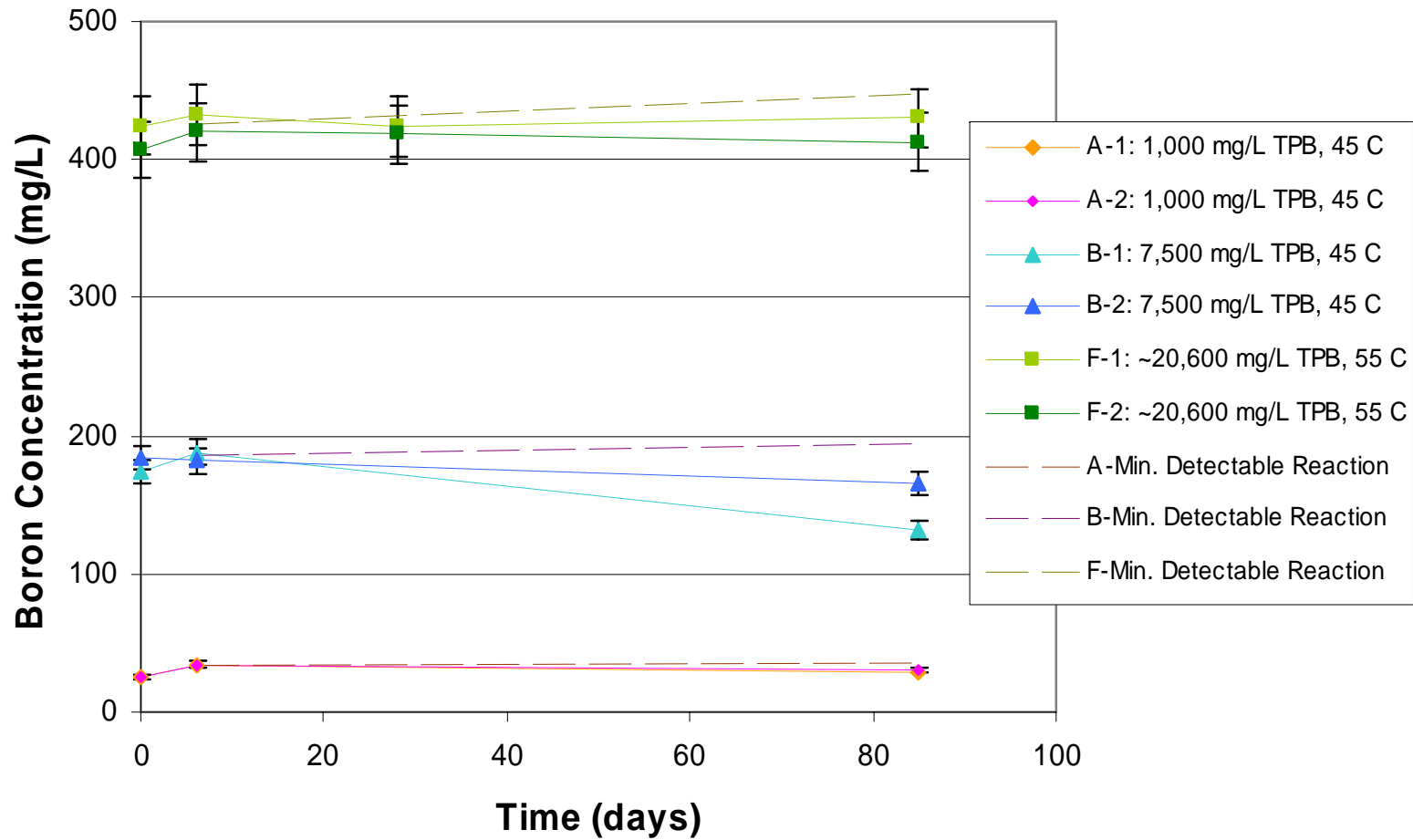


Figure 3. Graph of Boron Data



The analytical uncertainty of the boron measurements is 5% for all data points. Time=0 data point is at room temperature.

5.0 CONCLUSIONS

SRNL performed duplicate experiments at three different ratios of Tank 48H added to DWPF Recycle waste designed to determine if Tank 48H slurries at elevated temperatures would rapidly decompose the CsTPB and KTPB. This reaction, in turn, could generate benzene at too high a rate to handle safely. The added waste, when used, came from DWPF Recycle samples collected from Tanks 21H and 22H. In all three experiments, the TPB decomposition proved negligible, as determined by measurement of changes in concentration of ^{137}Cs , boron or potassium. The researchers noted a decline in the cesium activity in solution which is attributed to the increase in temperature (increase in temperature brings more TPB into solution which causes CsTPB to precipitate). Data from this work indicates that Tank 48H slurries, under these reaction conditions, even when mixed with DWPF recycle, exhibit negligible reaction at elevated temperatures of 45-55 °C for approximately 3 months.

7.0 REFERENCES

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