

# Sodium Tetrphenylborate Solubility and Dissolution Rates (U)

by

M. J. Barnes

Westinghouse Savannah River Company

Savannah River Site

Aiken, South Carolina 29808

R. A. Peterson

R. F. Swingle

C. T. Reeves

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## SODIUM TETRAPHENYLBORATE SOLUBILITY AND DISSOLUTION RATES (U)

### SUMMARY

The rate of solid sodium tetraphenylborate (NaTPB) dissolution in In-Tank Precipitation salt solutions has been experimentally determined. The data indicate that the dissolution rate of solid NaTPB is a minor contributor to the "lag time" experienced in the 1983 Salt Decontamination Demonstration Test and should not be considered as the rate determining step. Current analytical models for predicting the time to reach the composite lower flammability limit assume that the "lag time" is not more than 6 hours, and the data supports this assumption (i.e., dissolution by itself requires much less than 6 hours). The data suggests that another step -- such as mass transport, the reaction of a benzene precursor or the mixing behavior -- is the rate determining factor for benzene release to the vapor space in Tank 48H. In addition, preliminary results from this program show that the degree of agitation employed is not a significant parameter in determining the rate of NaTPB dissolution. As a result of this study, an improved equation for predicting equilibrium tetraphenylborate solubility with respect to temperature and sodium ion concentration has been determined.

### INTRODUCTION

Benzene and hydrogen gas will be produced during operation of the In-Tank Precipitation (ITP) process. Benzene is produced by the chemical and radiolytic decomposition of the tetraphenylborate salts. During the Salt Decontamination Demonstration Test in 1983, release of high levels of benzene was observed during the washing of concentrated slurry. Peak concentrations of benzene in the vapor space were observed within the six hour period following additions of water to the tank.<sup>1</sup>

Under normal operating conditions, the tank ventilation system keeps the concentration of benzene and hydrogen below the composite lower flammability limit (CLFL). However, any failure of the ventilation system could lead to an accumulation of a flammable gas mixture. During the peak release in the demonstration, the benzene release rate was sufficiently high that if Tank 48H had been without ventilation for an extended period of time, this release may have posed a flammability hazard. A model has been proposed to calculate the time needed to reach the CLFL in the absence of ventilation.<sup>2</sup> One particular concept included in the model is "lag time". The term "lag time" has been defined<sup>1</sup> as the period of time from the end of the water addition until after the peak benzene release is completed and the benzene release rate returns to that expected from free benzene generation only.

The process through which the release of benzene occurs due to the addition of water is complex. However, an understanding of this process can be gained by viewing it as a series of individual steps. A summary of these steps is as follows.

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The process through which the release of benzene occurs due to the addition of water is complex. However, an understanding of this process can be gained by viewing it as a series of individual steps. A summary of these steps is as follows.

<u>Step</u>	<u>Controlling Mechanism</u>
1. Water is added to Tank 48H.	Water Addition Rate
2.* The water is mixed with the slurry present in Tank 48H.	Mixing (Pump Speed)
3.* NaTPB dissolves.	Dissolution Kinetics
4.* Benzene dissolves or a precursor reacts to form benzene.	Reaction Kinetics
5.* Benzene is transported from the liquid phase (aqueous or insoluble benzene) to the vapor phase through the vapor-liquid interface.	Interfacial Mass Transfer

\* potential rate controlling step.

One variable central to the "lag time" concept is the rate of solid NaTPB dissolution during washing. It has been proposed that benzene, or a benzene precursor, is released from the crystal lattice of NaTPB as the solids dissolve. Benzene is produced by the radiolytic decomposition of solid NaTPB; the benzene, or a reactive precursor, is trapped by the rigid crystal lattice. Rapid dissolution of solid NaTPB would indicate the reaction kinetics of a benzene precursor or mass transfer could be limiting the benzene release rate to the vapor space. Alternatively, a slow NaTPB dissolution could control the benzene release rate. One objective of this study is to understand the role dissolution kinetics plays in benzene release.

Dissolution of solid NaTPB is driven during washing by the material's affinity for maintaining an equilibrium solubility concentration. Previous studies produced an equation for predicting NaTPB solubility in salt solutions as a function of temperature and sodium ion concentration.<sup>3</sup> This correlation is shown in Equation 1, where [NaTPB] is the solubility of NaTPB in molarity, T is the temperature in degrees Celsius, and X is the sum of the concentration of sodium ions from all salts, other than NaTPB, in molarity. The accuracy in predicting the NaTPB solubility and the factors affecting this value directly determine the reliability of any model for benzene release rates. As a result, High Level Waste Engineering (HLWE) has requested the Interim Waste Technology Section (IWTS) to investigate the evolution of benzene during washing in Technical Task Request HLE-TTR-95002.<sup>4</sup> Two objectives of this investigation include determining the rate of solid NaTPB dissolution in typical ITP salt solutions and improvement of the equation (Equation 1) predicting NaTPB solubility.

$$[NaTPB] = \left\{ \frac{0.86 + 0.0042(T)}{1 - 0.0026(T)} \right\} \{0.932e^{-1.23(X)}\}$$

(Equation 1)

## EXPERIMENTAL

The rate of solid NaTPB dissolution in ITP salt solutions, having sodium ion concentrations,  $[\text{Na}^+]$ , between 5.0 M and 0.2 M, was investigated. To perform this task, the dissolution rate of solid NaTPB in these solutions was studied in both a batch mode and during a continuous wash (i.e., dilution) under a range of conditions. The effects of  $[\text{Na}^+]$ , temperature, degree of mixing, and potassium tetrphenylborate (KTPB) solids on NaTPB solubility and the rate of dissolution of solid NaTPB were studied.

### Batch Dissolution Experiments

Batch dissolution experiments were conducted using salt solutions having varying sodium ion concentrations. The following procedure was used for each test. Equation 1 was used to estimate the equilibrium solubility concentration of NaTPB in the salt solutions. Depending upon the specific variables being tested (i.e., the effect of temperature, mixing, or KTPB), either 125% or 200% of the calculated soluble mass of NaTPB was added to glass volumetric flasks prior to the start of an experiment. To these solids, 100 mL of salt solution was added. The salt solutions tested had sodium ion concentrations ranging from 0.21 M to 5.0 M. These salt solutions were prepared by the dilution of a 6.1 M  $[\text{Na}^+]$  stock salt solution. This method permitted maintaining the same concentration ratio of individual components throughout the test. Table I shows the composition of this stock solution.

Aliquots of each test solution were taken periodically. Typically, the first sample was taken 15 minutes after the NaTPB solids and salt solutions were mixed. The aliquots were filtered immediately using either 0.2 or 0.45 micron syringe filter discs (both sizes were shown to perform equally well). Tetrphenylborate ion analysis of the aliquot samples was performed by the Analytical Development Section (ADS) using a silver ion/TPB<sup>-</sup> titration method.<sup>5</sup> A comparison of the results of this method of TPB<sup>-</sup> analysis with the results of a gravimetric analysis indicates that the error in this analysis is  $\pm 3.3\%$ . The sodium ion concentration was measured for each individual solution (prior to mixing with NaTPB) by ADS using inductively-coupled plasma (ICP) emission spectroscopy. The test solutions were maintained at a constant temperature using a water bath. Solutions were tested at 30 °C and 50 °C to probe the effect of temperature on NaTPB solubility. Unless otherwise noted, a vigorous degree of mixing (i.e., as much as permitted by the stirrers -- typically a vortex was present) was maintained in each solution using magnetic stirrers. However, there were two sets of tests that were not mixed with this degree of vigor. First, minimal agitation was required for the tests designed to study the effect of mixing on the rate of dissolution. In these specific tests, a gentle agitation of the solutions (i.e., a slow sloshing) was achieved by a motorized tray within the water bath. Second, only minimal agitation could be achieved in the tests incorporating 10 wt % KTPB solids due to the quantity of solids present. To conduct the KTPB solids tests, each test solution was spiked with approximately 10 g of washed, damp KTPB solids prior to addition to the experimental test flask.

### Continuous Washing Experiments

The current wash cycle proposed for the ITP process involves washing 10 wt % slurry over a period of 4 days. However, the test performed in 1983 employed a much shorter time period. Therefore, experiments were performed using two different time periods, 4 hours and 96 hours. Experiments were performed that simulate conditions in Tank 48H; solutions containing 1.5 and 3.0 wt % NaTPB solids

(these solutions represent 10 wt % solids with 15 and 30% excess NaTPB, respectively) were employed. Bulk salt solution was prepared as outlined in Table II. This salt solution was prepared without any potassium to facilitate the analysis of the tetraphenylborate solubility. To these solutions, 0.55 molar NaTPB was added as listed in Table III.

Solubility experiments were performed by adding wash water (deionized water) to the prepared slurry over a given period of time in a ratio of 625 mL of water for every 1000 mL of slurry. Samples were taken before and after the addition of the water and after the addition of half of the water. These samples were separated into two groups. One group of samples was immediately filtered using a 0.4 micron filter. The second group of samples were allowed to stand for a period of more than 4 days; then, these samples were also filtered. All of the samples were analyzed by ADS using a silver ion/TPB<sup>-</sup> titration method<sup>5</sup> to determine the amount of soluble NaTPB present. These slurry in these experiments was kept at 30 °C; the temperature of the wash water was room temperature (21 - 23 °C).

The variables studied were the total length of time employed and the weight percent excess NaTPB involved. An additional parameter that was studied was the effect of irradiation on the dissolution of NaTPB. The impact of irradiation was determined by performing one experiment with irradiated slurry under the conditions outlined above and employing the 4 hour time period for addition of water. All of the above experiments were carried out in a thoroughly mixed vessel. One experiment was carried out in an unmixed vessel.

Table I. Composition of stock salt solution used to prepare individual batch dissolution test solutions.

Component	Concentration
Total Na <sup>+</sup>	6.06 M
NaOH	1.60 M
NaAl(OH) <sub>4</sub>	0.35 M
NaNO <sub>3</sub>	2.52 M
NaNO <sub>2</sub>	0.85 M
Na <sub>2</sub> CO <sub>3</sub>	0.20 M
Na <sub>2</sub> SO <sub>4</sub>	0.15 M

Table II. Concentrations of various components in the salt stream representative of 3.0 wt % and 1.5 wt % excess.

Component	Grams/Liter 1.5 wt %	Moles/Liter 1.5 wt %	Grams/Liter 3.0 wt %	Moles/Liter 3.0 wt %
NaOH	113.0	2.82	122.7	3.06
Al(NO <sub>3</sub> ) <sub>3</sub> •9H <sub>2</sub> O	123.7	0.33	134.3	0.36
NaNO <sub>3</sub>	103.3	1.21	112.2	1.25
NaNO <sub>2</sub>	53.3	0.77	57.9	0.84
Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O	22.6	0.18	24.5	0.20
Na <sub>2</sub> SO <sub>4</sub>	20.9	0.14	22.7	0.15

Table III. NaTPB solution requirements.

Experiment Identification	Volume of 0.55 M NaTPB Solution Required (mL/liter of salt solution)
1.5 wt %	106
3.0 wt %	212

## RESULTS AND DISCUSSION

### Batch Dissolution Experiments

Batch dissolution experiments were conducted in support of continuous wash tests. Batch dissolution tests are easier to conduct than the continuous wash experiments and more variables may be tested with less difficulty. The batch dissolution experiments were designed to gauge the rate that equilibrium solubility of tetraphenylborate is achieved relative to the solution environment. Individual sets of tests were performed in which similar solutions with varying sodium ion concentrations were subjected to two different temperatures (30 °C and 50 °C), two different degrees of mixing (vigorous and gentle agitation), and the presence of 10 wt % KTPB solids. Data from these experiments are presented in Tables IV, V, VI, and VII.

Table IV lists the data from experiments performed at 30 °C with vigorous mixing by magnetic stirrers. Table V contains the data from experiments performed at 30 °C with gentle agitation (i.e., a slow sloshing of the solution controlled by movement of a tray in the water bath). Table VI lists the data collected at 50 °C with gentle agitation. Table VII contains data from experiments performed with salt solutions containing approximately 10 wt % KTPB solids at 30 °C. Due to the high loading of solids, only minimal agitation was possible in the presence of KTPB.

Comparison of Tables IV and VI demonstrate that solubility of NaTPB in salt solutions increases with increased temperature. The rate of dissolution, however, is affected very little by the change in temperature. At both 30 °C and 50 °C, the NaTPB concentration reached a maximum within 1 hour, and in most cases within about 15 minutes. A comparison of the equilibrium concentration of NaTPB at the two temperatures is presented in Figure 1.

To study the effect of agitation on the dissolution rate, experiments were performed at 30 °C in which one set of solutions was strongly mixed using magnetic stirrers and one set was gently agitated. Comparison of the data (Tables IV and V) shows that there is no difference in the dissolution rate between solutions that were vigorously stirred and those that were gently agitated. However, the design of the experiments did not allow for precise control over the degree of mixing. The experiments were designed so that the salt solutions were added to containers that held the NaTPB powder; a good deal of mixing occurred in the gently agitated solutions during the addition of the salt solutions.



The presence of 10 wt % KTPB solids in the solutions did not affect the rate of NaTPB dissolution (Table VII). However, the NaTPB equilibrium solubilities for the individual solutions was more scattered and biased slightly (~ 20%) high in comparison to the data in Table V. Furthermore, the data contained in Table VII indicates that the solutions became supersaturated with tetraphenylborate. Over time (24 days) the tetraphenylborate concentration did equilibrate.

Table IV. NaTPB Concentration as a function of time and sodium ion concentration,  $[\text{Na}^+]$ , in solutions at 30 °C with strong mixing.

Reaction Time	Tetraphenylborate Ion Concentration (M)								
	5.0 M $[\text{Na}^+]$	2.34 M $[\text{Na}^+]$	1.99 M $[\text{Na}^+]$	1.81 M $[\text{Na}^+]$	1.50 M $[\text{Na}^+]$	1.25 M $[\text{Na}^+]$	0.99 M $[\text{Na}^+]$	0.50 M $[\text{Na}^+]$	0.21 M $[\text{Na}^+]$
0.25 hr	< 0.002	0.067	0.090	0.110	0.161	0.229	0.317	0.539	0.710
0.50 hr	-	-	0.097	0.131	0.135	0.232	-	0.532	0.710
1 hr	< 0.002	0.067	0.101	0.130	0.174	0.233	0.330	0.532	0.710
2 hr	-	-	0.096	0.130	0.173	0.233	0.330	-	-
4 hr	< 0.002	0.067	0.096	0.130	0.174	0.229	0.310	-	-
6 hr	-	-	-	-	-	-	0.314	-	-
1 day	< 0.002	0.068	0.095	0.130	0.171	0.225	0.314	0.565	0.691
2 days	< 0.002	0.068	-	-	-	-	0.316	0.529	0.712
3 days	-	-	-	-	-	-	-	-	-
4 days	< 0.002	0.070	-	-	-	-	0.326	0.533	0.698
6 days	-	-	0.095	0.129	0.173	0.231	-	-	-
7 days	< 0.002	0.073	-	-	-	-	-	-	-

Table V. NaTPB Concentration as a function of time and sodium ion concentration,  $[\text{Na}^+]$ , in solutions at 30 °C with gentle agitation.

Reaction Time	Tetraphenylborate Ion Concentration (M)								
	5.0 M $[\text{Na}^+]$	2.34 M $[\text{Na}^+]$	1.99 M $[\text{Na}^+]$	1.81 M $[\text{Na}^+]$	1.50 M $[\text{Na}^+]$	1.25 M $[\text{Na}^+]$	0.99 M $[\text{Na}^+]$	0.50 M $[\text{Na}^+]$	0.21 M $[\text{Na}^+]$
0.25 hr	< 0.002	0.068	0.096	0.133	0.172	0.218	0.314	0.533	0.699
0.50 hr	-	-	0.099	0.128	0.173	0.228	-	0.527	0.705
1 hr	-	-	0.096	0.130	0.173	0.227	0.330	0.528	0.711
2 hr	-	-	0.097	0.129	0.171	0.230	0.326	-	-
4 hr	< 0.002	0.068	0.097	0.129	0.172	0.231	0.322	0.531	0.704
1 day	< 0.002	0.073	0.096	0.130	0.173	0.231	0.315	0.531	0.702
2 days	< 0.002	0.070	-	-	-	-	0.326	-	-
4 days	< 0.002	0.070	-	-	-	-	0.329	0.533	0.693
6 days	-	-	0.098	0.131	0.173	0.234	-	-	-
7 days	< 0.002	0.069	-	-	-	-	-	-	-

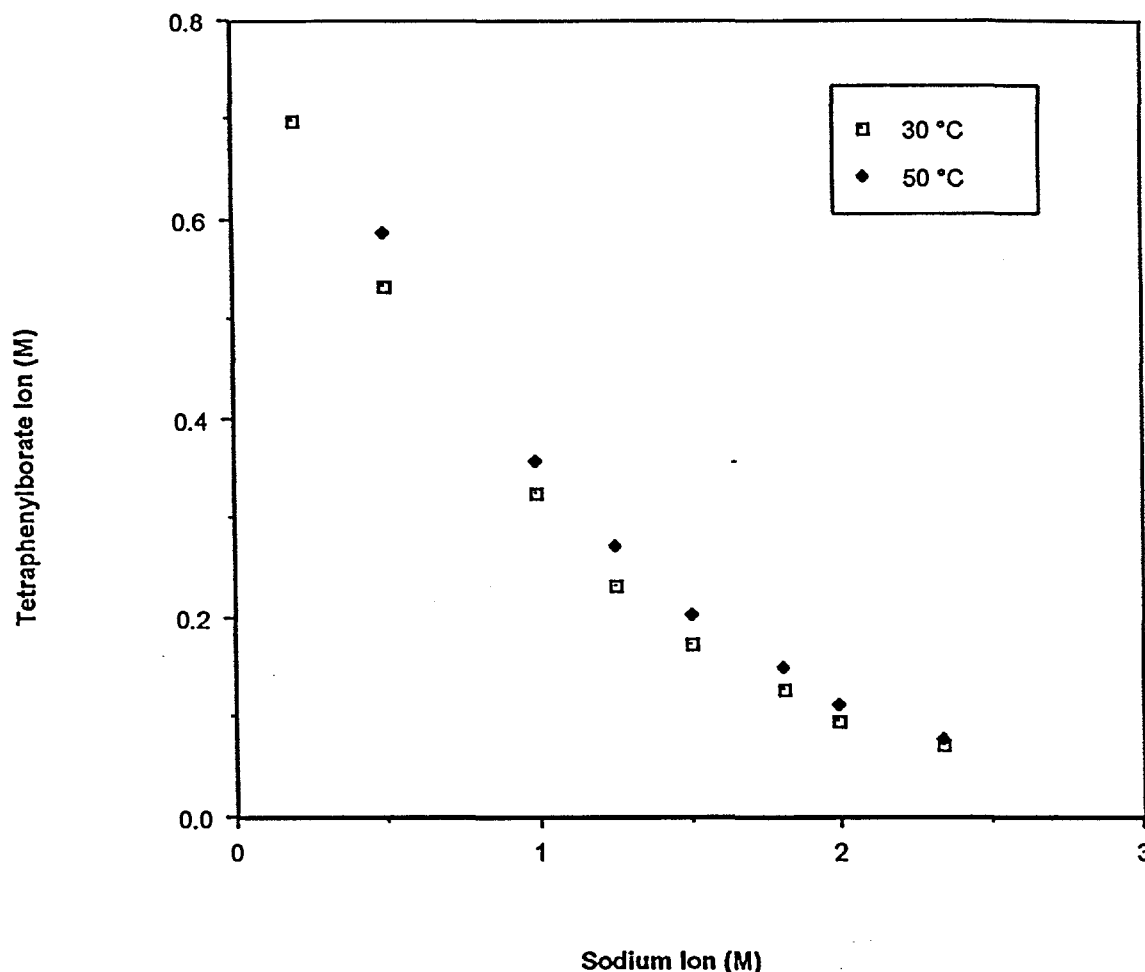
Table VI. NaTPB Concentration as a function of time and sodium ion concentration,  $[\text{Na}^+]$ , in solutions at 50 °C with gentle agitation.

Reaction Time	Tetraphenylborate Ion Concentration (M)							
	5.0 M $[\text{Na}^+]$	2.34 M $[\text{Na}^+]$	1.99 M $[\text{Na}^+]$	1.81 M $[\text{Na}^+]$	1.50 M $[\text{Na}^+]$	1.25 M $[\text{Na}^+]$	0.99 M $[\text{Na}^+]$	0.50 M $[\text{Na}^+]$
0.25 hr	0.002	0.072	0.110	0.146	0.199	0.272	0.366	0.636
0.50 hr	-	-	0.110	0.111	0.199	0.263	0.344	-
1 hr	-	-	0.110	0.150	0.199	0.263	0.343	-
2 hr	-	-	0.112	0.150	0.202	0.266	0.355	-
4 hr	0.003	0.075	0.113	0.145	0.195	0.263	0.346	0.597
1 day	0.003	0.075	0.109	0.151	0.201	0.268	0.360	0.618
2 days	0.002	0.075	-	-	-	-	-	-
7 days	0.002	0.076	0.113	0.150	0.204	0.271	0.357	0.587

Table VII. The effect of 10 wt % KTPB solids on NaTPB concentration as a function of time and sodium ion concentration,  $[\text{Na}^+]$ , in solutions at 30 °C with minimal agitation.

Reaction Time	Tetraphenylborate Ion Concentration (M)							
	2.68 M $[\text{Na}^+]$	2.48 M $[\text{Na}^+]$	1.83 M $[\text{Na}^+]$	1.69 M $[\text{Na}^+]$	1.45 M $[\text{Na}^+]$	1.17 M $[\text{Na}^+]$	1.01 M $[\text{Na}^+]$	0.85 M $[\text{Na}^+]$
0.25 hr	0.040	0.066	0.199	0.269	0.342	0.457	-	0.602
0.50 hr	0.043	0.065	0.199	0.269	0.339	0.430	0.528	0.567
1 hr	0.040	0.064	0.195	0.265	0.336	0.451	0.507	0.582
4 hr	0.037	0.060	0.187	0.250	0.323	0.432	0.491	0.555
1 day	0.036	0.058	0.190	0.239	0.308	0.418	0.480	0.524
5 days	0.029	0.050	0.177	0.223	-	-	-	-
6 days	-	-	-	-	0.287	0.396	0.451	0.513
13 days	0.027	0.050	0.169	0.213	-	-	-	-
14 days	-	-	-	-	0.285	0.388	0.436	0.489
24 days	-	-	-	-	0.279	0.380	0.441	0.490

Figure 1. Solubility of tetraphenylborate ion as a function of sodium ion concentration and temperature.



### Continuous Washing Experiments

Further information can be gathered by investigating the instantaneous and equilibrium solubility of solutions that originally contained 1.5 wt % and 3.0 wt % NaTPB. These results are presented in Figures 2 and 3. The data represent both fast and slow addition rates (over either 96 or 4 hours). No significant difference was observed between the instantaneous solubilities or the equilibrium solubilities or as a function of the rate of addition. There is a significant scatter in the experimental data. The reader should note that the data presented in Figures 2 and 3 include two experimental variations. Figure 2 includes one experiment with irradiated slurry that contained 1.5 wt % NaTPB; Figure 3 includes one experiment that was not mixed. The solubilities reported from these two experiments fell within the scatter of the data. (See Table VIII for additional information.)

Figure 2. Instantaneous and equilibrium solubility of tetraphenylborate ion (with initial 1.5 wt % excess solid NaTPB) as a function of the rate of dilution.

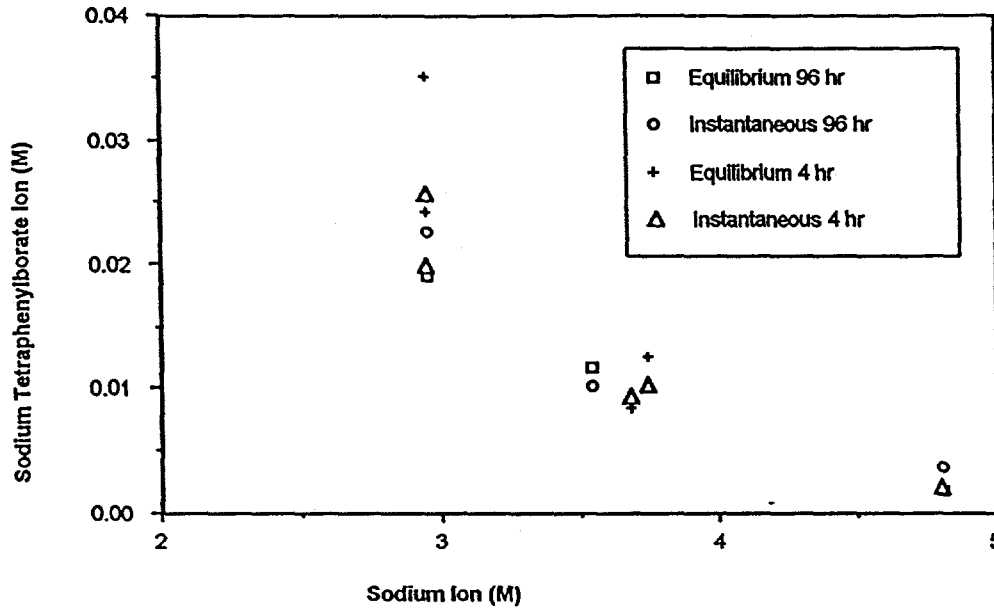


Figure 3. Instantaneous solubility of tetraphenylborate ion (with a 3.0 wt % excess solid NaTPB) as a function of the rate of dilution.

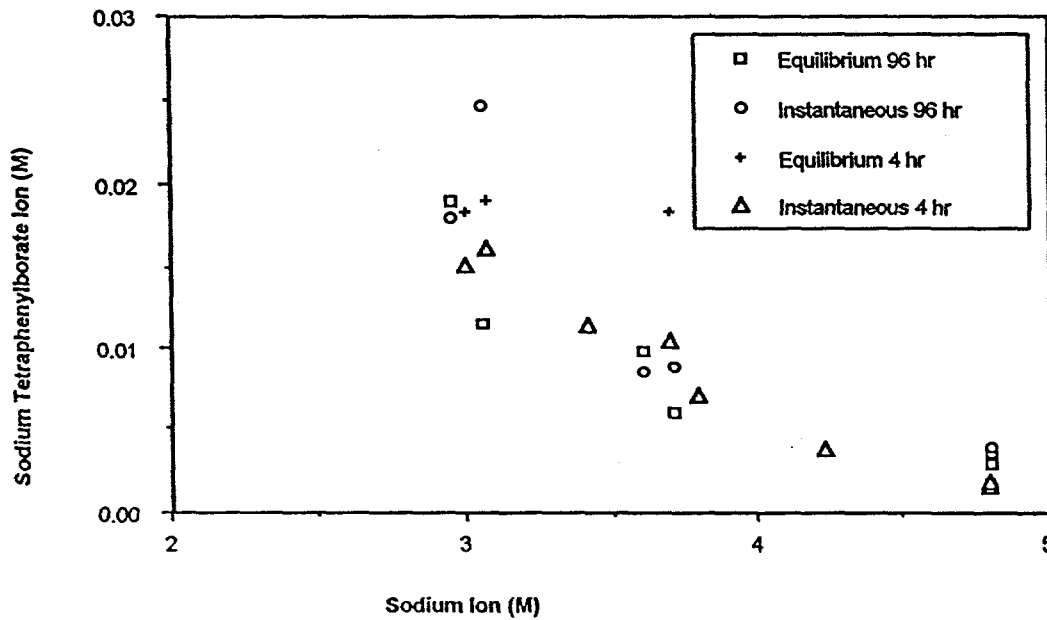


Table VIII. NaTPB Concentration as a function of sodium ion concentration and addition rate.

Initial Percent Excess	Molarity (Na)	Duration of Water Addition (hr)	Instantaneous TPB Concentration(M)	Equilibrium TPB Concentration(M)
1.5	4.8	4	0.0015	0.0020
	4.8*	4	0.0018	0.0019
	3.8	4	0.007	0.007
	3.7*	4	0.0104	0.0076
	3.1	4	0.016	0.019
	3.0*	4	0.015	0.018
	4.8	96	0.0017	0.003
	4.8	96	0.0039	0.0039
	3.7	96	0.0089	0.0065
	3.6	96	0.0086	0.0099
	3.05	96	0.0247	0.0116
	2.95	96	0.018	0.019
3.0	4.8	4	0.002	0.002
	4.8**	4	0.002	0.0021
	3.75**	4	0.0103	0.0125
	3.7	4	0.094	0.0084
	2.95**	4	0.0199	0.0349
	2.95	4	0.0256	0.0241
	4.8	96	0.0038	0.0019
	3.5	96	0.0103	0.0117
	2.95	96	0.0227	0.019

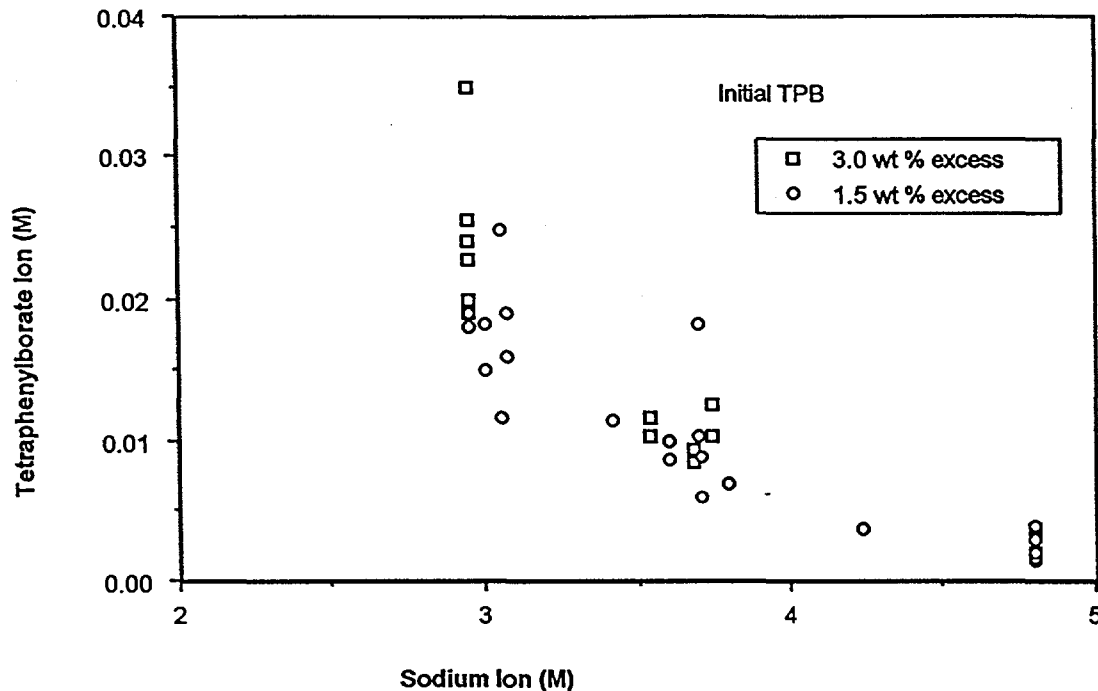
\* Irradiated slurry.

\*\* Without mixing.

One of the primary results that can be gathered from these experimental protocols concerns the equilibrium solubility of NaTPB as a function of the sodium ion concentration. These results are presented in Figure 4. The data in Figure 4 are distinguished into two groupings according to the initial percentage of NaTPB. As the sodium molarity is decreased below 3.5 M, the scatter of the data increases significantly.

A partial explanation of this phenomena can be proposed. Under the experimental conditions employed, the slurry that initially contained 1.5 wt % excess NaTPB has little solid NaTPB at sodium concentrations near 3.0 M. All of the solid phase NaTPB can be dissolved by diluting the sodium ion concentration to 2.8 M. Thus, a partial explanation for the discrepancy in the data presented in Figure 4 can be attributed to the proximity of the low concentration slurry to its solubility limit (i.e., that under the conditions measured, all of the NaTPB may be soluble). The standard deviations of these mean values of the measurements at 3.0 M sodium ion concentration are 0.004 M and 0.008 M for the 1.5 and 3.0 wt % samples, respectively. The sum of these standard deviations is larger than the difference between the mean values (~ 0.008 M). Thus, the variability of the measurements themselves may account for most of the separation of these data points.

Figure 4. Solubility of tetraphenylborate ion as a function of sodium ion concentration and excess solid NaTPB.



### Sodium Tetraphenylborate Solubility Equation

An additional objective of this investigation included revisiting the existing equation for predicting NaTPB solubility. The original equation for predicting NaTPB solubility<sup>3</sup> is shown as Equation 1 in the Introduction section of this report. This equation was derived from data given in Table IX.<sup>6</sup> A new equation has been derived from equilibrium NaTPB solubility data given in Tables IV, VI, VIII and IX using version 5 of the STATGRAPHICS<sup>®</sup> computer program. The data was fit to a logarithmic form of an equation similar to Equation 1 using the STATGRAPHICS<sup>®</sup> nonlinear regression routine. The logarithmic form of the equation was used to fit the data so that the low NaTPB concentration data would be better utilized. The following equation resulted.

$$[NaTPB] = \left\{ \frac{0.684 + 0.00324(T)}{1 - 0.00324(T)} \right\} \left\{ 1.08e^{-1.22(x)} \right\} \quad (\text{Equation 2})$$

The nomenclature for the variables is the same as that given for Equation 1.

A statistical analysis was done on both of the equations. Equation 1 was compared to the original data used to generate the equation (Table IX) and to the equilibrium data used to generate Equation 2 (Tables IV, VI, VIII and IX). Equation 2 was compared only to all of the data used to generate the

equation. Values for the standard deviation,  $\sigma$ , and for the percent relative standard deviation were calculated for each of the cases described above. The following equations were used to calculate these values.

$$\sigma = \sqrt{\left( \frac{\sum_{i=1}^n (y_{calc,i} - y_{exp,i})^2}{n} \right)}$$

(Equation 3)

$$\%RSD = \left[ \frac{\sum_{i=1}^n (y_{calc,i} - y_{exp,i}) / y_{exp,i}}{n} \right] \times 100$$

(Equation 4)

where  $y_{calc,i}$  = the value of [NaTPB] as calculated using the equation being tested,  
 $y_{exp,i}$  = the experimental value of [NaTPB] and  
 $n$  = the number of data points in set being analyzed.

The original equation (Equation 1) gave a  $\sigma$  of 0.0068 and a relative standard deviation of 21.6% when compared to the data from which it was derived (Table IX). A  $\sigma$  of 0.0195 and a relative standard deviation of 24.1% were obtained when Equation 1 was compared to all of the data. When Equation 2 was compared to all of the data, a  $\sigma$  of 0.0152 and a relative standard deviation of 23.5% were obtained. The residuals of the two models are shown in Figure 5. This figure shows that there is very little difference in the magnitude of the residuals between the NaTPB concentrations calculated by Equations 1 and 2 and the experimental data. Figure 6 shows that the relative standard deviation for the two models is approximately the same for all data points. The relative standard deviation is also shown to increase with increasing sodium ion concentration (i.e., with decreasing NaTPB concentration). Figure 5 shows that at sodium ion concentrations above 3 M, both models do an equally good job of predicting NaTPB solubility. However, at lower sodium ion concentrations, the Equation 1 model slightly underpredicts the NaTPB solubility, while Equation 2 slightly overpredicts the NaTPB solubility.

**Table IX.** NaTPB concentration as a function of sodium ion concentration and temperature, data used to derive Equation 1.

Temperature (°C)	Sodium Ion Molarity	NaTPB Concentration (M)
21	0	0.89
21	0	0.924
68	0	1.24
68	0	1.25
68	0	1.25
23	0.1	0.795
23	3.11	0.032
23	3.44	0.014
23	3.71	0.0125
23	3.91	0.0087
23	4.3	0.0065
23	4.68	0.004
23	5.29	0.0008
23	5.5	0.0018
23	6.9	0.0002
23	6.9	0.0011

**Figure 5.** Residuals between actual tetraphenylborate solubility data and results predicted by Equations 1 and 2.

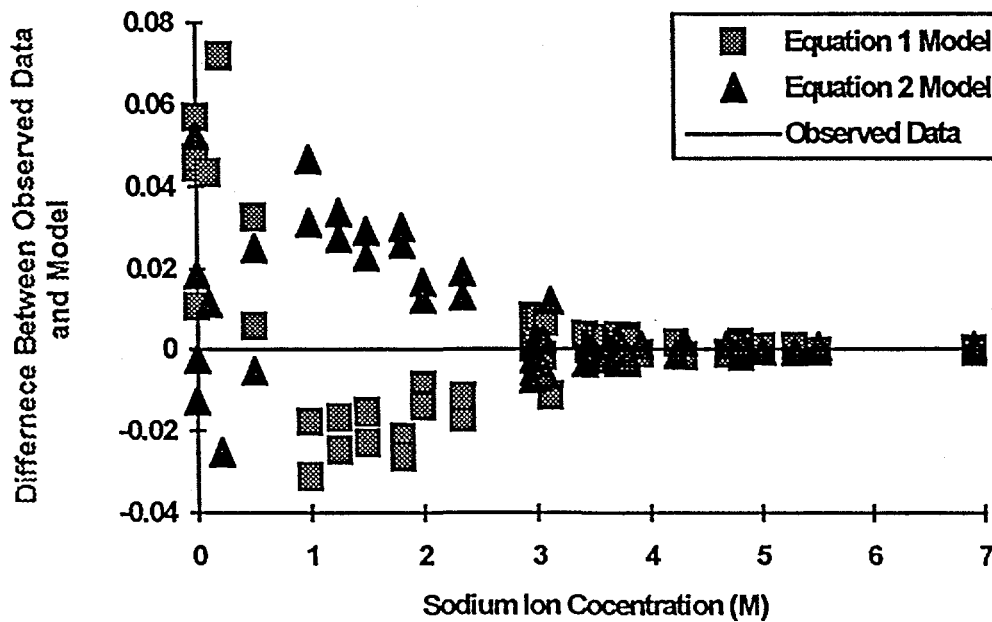
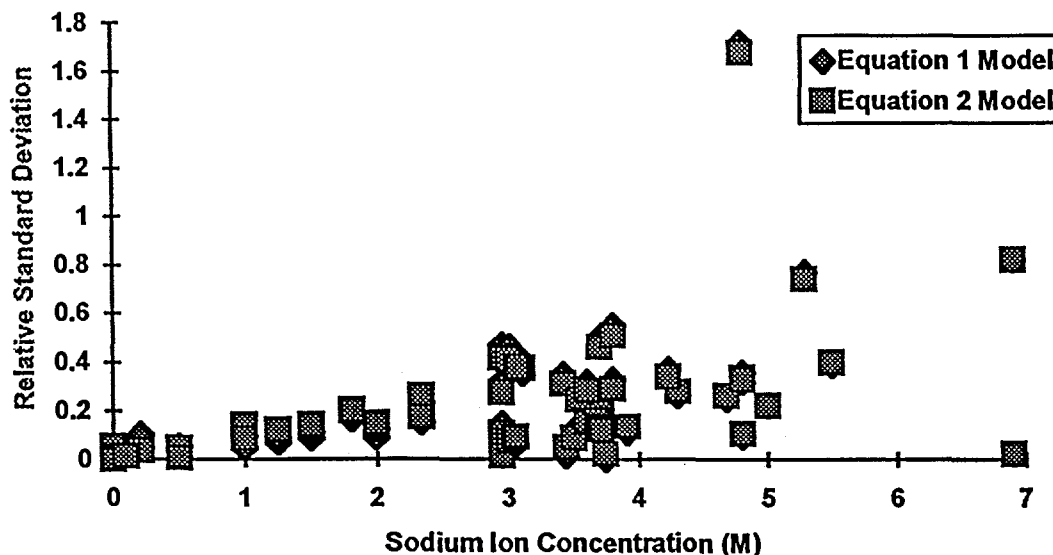




Figure 6. Relative Standard Deviation for the two models.



## CONCLUSIONS

Examination and comparison of the data obtained in this study results in the following conclusions which are valid regardless of the test conditions employed.

- The sodium ion concentration of a test solution does not affect the rate of NaTPB dissolution. In the test solutions, the majority of tetraphenylborate dissolved within 15 minutes of the start of the tests and reached an equilibrium concentration in an hour or less.
- Preliminary results from this program show that the degree of agitation employed is not a significant parameter in determining the rate of NaTPB dissolution.
- As expected, the NaTPB solubility limit for a particular solution is dominated by the sodium ion concentration of the solution.
- The presence of 10 wt % KTPB solids does not reduce the rate of NaTPB dissolution. In fact, the data indicates that up to 20% supersaturation occurs initially. Over 24 days the tetraphenylborate concentration did equilibrate.
- Irradiation does not produce any discernible changes in the dissolution rate.

In summary, the data indicate that the dissolution rate of solid NaTPB is a minor contributor to the "lag time" concept in the benzene generation model. The model assumes that the "lag time" is not more than 6 hours, and the data supports this assumption (i.e., dissolution by itself does not require more than 6 hours). The data suggests that another variable such as mass transport or the presence of a benzene precursor is controlling the benzene release rate to the vapor space in Tank 48H.

While the data has indicated that the dissolution of NaTPB is complete within the 6 hour "lag time", it is unclear at this time how the other two mechanisms outlined will contribute to the determination of the "lag time". Thus, it may prove desirable to perform additional experiments aimed at illuminating this subject. One set of experiments that could be performed would be to measure the mass transfer coefficients within the slurry to determine the impact of mass transfer limitations on the "lag time". Another set of experiments would involve identifying a reaction pathway by which benzene is formed and determining the reaction rates for the necessary reaction steps. These determinations would shed additional light on the length of the "lag time".

As an additional result of this program, a new equation for predicting equilibrium tetraphenylborate solubility with respect to temperature and sodium ion concentration has been determined.

#### QUALITY ASSURANCE

All work was conducted in accordance with the DWP&HT Quality Assurance Procedures Manual, 1Q43. The experimental procedures and data collected during this program are contained in laboratory notebooks WSRC-NB-94-271 and WSRC-NB-94-311. This experimental program was conducted at the request of HLWE. Documents relevant to this request include HLE-TTR-95002<sup>3</sup>, WSRC-RP-94-1153<sup>7</sup> and WSRC-RP-95-223.<sup>8</sup>

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