# Cesium, Potassium, and Sodium Tetraphenylborate Solubility In Salt Solution

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Cesium, Potassium, and Sodium Tetraphenylborate Solubility in Salt Solution (U)

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#### Summary

Use of sodium tetraphenylborate to precipitate cesium in the In-Tank Precipitation (ITP) process results in the potential for benzene formation. Using lesser amounts of the chemical reduces the potential for forming benzene. The resulting lower flammability risk increases the safety margin for operations. This report documents studies of the solubility of cesium, potassium, and sodium tetraphenylborate. Increased understanding of the solubility allows reduced usage.

- The solubility product constant  $(K_{sp})$  of potassium tetraphenylborate (KTPB) determined in this task agrees with that observed in previous published studies.
- The solubility product constant of CsTPB has been determined, and agrees with the 1983 In-Tank Demonstration data.
- The solubility of CsTPB increases approximately 10-fold with a temperature rise from 25 to 65 °C.
- The solubility product constant of CsTPB determined in this task is approximately 10% of that observed in published studies. The discrepancy is due to differences in the K:Cs ratio.
- The ratio of potassium to cesium impacts the solubility of CsTPB in salt solutions. More research is needed to quantify the effect.
- At <1.5 M sodium ion concentration, the CsTPB precipitation reaction is complete in less than 24 hours for stoichiometric additions of TPB<sup>-</sup> at 25 °C.
- Above 1.5 M sodium ion concentration, the CsTPB precipitation reaction time can reach 160 hours at 25 °C. Addition of excess tetraphenylborate and higher temperature speeds the precipitation.
- Organics (i.e., phenol, benzene, phenylboric acid) do not impact the solubility of cesium in alkaline solutions with tetraphenylborate at the concentrations observed in ITP.
- If the activity coefficients are corrected for the variability in composition, the ratios of the anions (sulfate, nitrate, etc.) do not significantly impact the solubility of CsTPB in these solutions.

Equation 1

#### Introduction

The ITP Process decontaminates radioactive waste in Tank 48H by precipitating cesium with sodium tetraphenylborate (NaTPB) and adsorbing radioactive strontium on MST. In addition to the cesium, all of the potassium in the solution precipitates with the TPB<sup>-</sup>. The solids are separated from the salt solution by crossflow filters. The design basis for removal of radioactive materials is to achieve less than 30 nCi/g of Cs-137 and less than 18 nCi/g of alpha emitters in the filtrate. The cesium removal requirement is achieved by the extremely low solubility of cesium tetraphenylborate. The use of the tetraphenylborate (TPB<sup>-</sup>) ion for precipitation of radioactive cesium from High Level Waste (HLW) suffers from generation of benzene. To achieve the high decontamination factor, excess NaTPB is added to the solution to force the cesium out of solution. The "excess" TPB<sup>-</sup> concentration causes cesium to precipitate and restore equilibrium (Equation 1).

 $Cs^{+}_{(AQ)} + TPB^{-}_{(AQ)} < ----> CsTPB_{(solid)}$ 

Decreasing the excess NaTPB reduces the potential quantity of benzene produced. To decrease the concentration of NaTPB while maintaining the cesium decontamination factor requires an accurate description of the factors influencing the solubility cesium tetraphenylborate (CsTPB) and potassium tetraphenylborate(KTPB). In support of the Defense Nuclear Facility Safety Board (DNFSB) Recommendation 96-1 Implementation Plan,<sup>1</sup> High Level Waste Engineering requested a study of the solubility of tetraphenylborate salts of cesium and potassium.<sup>2</sup>

Previous equations used to calculate the CsTPB and NaTPB solubility<sup>3</sup> were based on work by E. Siska.<sup>4</sup> These equations were not consistent with observations during testing and demonstration of the ITP process. Further testing has been completed to determine the equations that more accurately predict the solubility of CsTPB, NaTPB, and KTPB.

The equilibrium solubility product constant of CsTPB can be described by equation 2.

 $K_{sp(Cs)} = [Cs^+] [TPB^-] \times (\gamma_{Cs}) \times (\gamma_{TPB})$  Equation 2

Where  $[Cs^+]$  and  $[TPB^-]$  are the molar concentrations of the aqueous species and  $\gamma_{cs}$  and  $\gamma_{TPB}$  are the molality-scale activity coefficients The activity coefficients are described by the Debye-Hückle equation<sup>5</sup> for dilute solutions, but must be adjusted for the ionic strength for more concentrated solutions (>0.01 m). One method for calculating the activity coefficients is use of a computer software model, Environmental Simulation Program by OLI, Inc. This software utilizes a mathematical framework to derive the thermodynamic properties of aqueous solutions.

#### Experimental

Simulated salt solutions were prepared at 4.7 M  $[Na^{+}]$  (Table 1). The standard solution was diluted with deionized water to achieve the desired sodium concentration for specific tests. For solutions containing less than 1.0 M [Na<sup>+</sup>], aliquots of cesium nitrate and potassium nitrate solutions were added to maintain the concentrations above the solubility product. The ratio of cesium to potassium remained constant (at 1:62) unless otherwise specified. Simulants for NaTPB solubility were prepared without cesium or potassium nitrate. Simulants were also prepared from sodium sulfate for comparison to literature data. Cesium nitrate and potassium nitrate were also added to these solutions. Sodium tetraphenylborate (Aldrich, 99+%) solution (0.5 M, 4/2/96 ITP Benzene Tests Solution A) was added to the salt solutions and the samples were continuously agitated at 150-200 rpm for 24 hours (unless otherwise specified in kinetics tests). Solid sodium tetraphenylborate (Aldrich, 99+%) was used for the NaTPB solubility tests.

Ta:	b]	le	1.	4.	7	M	[Na+]	Aqueous	Salt	Solution	
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Component	<u>Concentration (M)</u>
Na <sub>2</sub> SO <sub>4</sub>	0.14
NaNO <sub>2</sub>	0.66
NaNO3	0.74
NaOH KNO <sub>3</sub>	2.68 (1.4 M free OH 0.013
Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O	0.17
Al (NO <sub>3</sub> ) $_3 \cdot 9H_2O$ CsNO <sub>3</sub>	0.32 0.00021

Selected organic compounds present in decomposed tetraphenylborate slurry were added to one simulated salt solution to examine their impact. The solution was diluted to 0.25 M  $[Na^+]$  and 1000 mg/L each of phenol, phenylboric acid, and benzene were added. The phenylboric acid and phenol completely dissolved.

A simulated salt solution containing different ratios of anions were also prepared to examine the effect of anion composition. The solution did not contain any divalent anions (Table 2). The solution was prepared at 5.6 M [Na+] and diluted to the desired concentration (0.25 M [Na<sup>+</sup>]) prior to NaTPB addition.

#### Table 2. 5.6 M [Na+] High Hydroxide Salt Solution

Component	Concentration (M)
NaNO <sub>2</sub>	0.30
NaOH	5.3 (2.26 M free OH)
KNO3	0.015
Al (NO3) 3.9H2O	0.76
CsNO3	0.00024

Temperature of the slurries was maintained using an orbital shaking water bath. Temperature of the water was recorded and found to vary by  $\pm 2.5$  °C. All CsTPB and KTPB samples were filtered with 0.2 micron Nalgene<sup>TM</sup> filters. The NaTPB samples were filtered with 0.45 micron Nalgen<sup>TM</sup> filters. For the elevated temperature tests, samples were filtered quickly (<2 minutes) and ultrapure water was added to maintain the solubility of the compounds as it cooled. The ultrapure water was checked by Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS) and found to not contain measurable amounts of K, Cs, or B.

All samples were analyzed by ICP-MS. The boron purity of the NaTPB was examined by addition of NaTPB to a 1.0 M potassium nitrate solution. Less than 0.064 % of the added boron was found soluble after precipitation of KTPB, indicating that boron analysis could determine the TPB<sup>-</sup> concentration.

Blank samples (i.e., no NaTPB added) were analyzed for with each series of samples to confirm the accuracy of the analyses. Also, a series of blind standards were prepared and analyzed. The blind standard was prepared from the same batch of reagent grade chemicals as the simulant. The calculated versus measured concentrations were within the expected error of ~10% (Figures 1 and 2).

Densities of the solutions after NaTPB addition were determined over a range of concentrations (Table 3). The amount of NaTPB added to these solutions was stoichiometrically equivalent to the concentration of potassium and was not saturated with NaTPB. A pipetter was used to measure the volume of salt solution and the pipetter was checked with a weighed amount of deionized water to ensure a consistent volume delivery. The densities were measured in triplicate. The molality (m) of the solutions were then calculated from the density (Table 3, Figure 3) and composition.

#### Table 3. Density of Salt Solutions (T = 25 $^{\circ}$ C)

Na (M)	density (g/mL)	<u>Na (m)</u>
4.7	1.2179	5.2
1.4	1.0715	1.5
0.47	1.0248	0.47
0.14	1.0144	0.14
0.047	1.0063	0.047

#### <u>Results and Discussion</u>

#### Precipitation Kinetics

The precipitation of CsTPB in 0.28 M sodium ion salt solution is complete in less than 24 hours at room temperature (Table 4, Figure 4) with stoichiometric quantities of potassium and tetraphenylborate ions (± 1%). The cesium concentration increased after 216 hours and is likely attributable to variability in the experimental procedure or the analysis. The standard deviations calculated for this test reflect the variance for replicate experiments. Temperature, homogeneity of samples, pipette volumes, and analytical scatter contribute to this variance. The cesium concentration is near the detection limit of the instrument, contributing to the variability of the data. A longer test is needed to confirm that the results are due to experimental variability.

#### Table 4. Precipitation Kinetics in 0.28 M [Na<sup>+</sup>] at 25 °C

Time	(hr)	Kspl (CsTPB)	Ksp2 (KTPB)
24		1.00E-10	3.94E-8
72		9.21E-11	4.06E-8
144		1.10E-10	3.78E-8
216		1.65E-10	4.36E-8
	average	1.17E-10	4.04E-8
	std. dev.	3.29E-11	2.48E-9

At 4.7 M sodium ion salt solution with near-stoichiometric addition of TPB, the reaction was nearly complete after approximately 160 hours (Figure 5) at 25 °C. The solution contained less TPB<sup>-</sup> than the stoichiometric amount of potassium  $(0.198 \text{ mM } [K^+] \text{ vs. } 0.145 \text{ mM } [TPB^-])$  due to tramp potassium in the chemicals used to prepare the simulant, yielding a conservative estimate of the reaction time. This caused a higher cesium solubility in these samples, consistent with a shift in the equilibrium. This data indicates that the precipitation reaction at near-stoichiometric conditions in high ionic strength solutions can be very slow. Further work is needed to precisely define the precipitation kinetics with excess TPB<sup>-</sup>.

At 4.7 M sodium ion salt solution at 65 °C with nearstoichiometric addition of TPB, the reaction was complete in 24 hours (Figure 6). The results indicate that the time required for precipitation can be significantly reduced by heating the solution; however, the solubility also increases with temperature.

At 1.41 M [Na<sup>+</sup>] and 25 °C, the reaction was complete in less than four hours (Figure 7). The cesium concentration was below the detection limit when the first sample was collected, indicating a very rapid reaction. Further work is needed to quantify the impact of excess TPB<sup>-</sup> on the precipitation rate.

#### Equilibrium Constant Calculation

Equations for the cation  $(K^*, Cs^*, Na^*)$  and anion  $(TPB^-)$  activity coefficients in salt solution have been derived from the Environmental Simulation Program by OLI, Inc. The equations were then used as a basis for experiments. To determine if the activity coefficients were valid, the solubility of the tetraphenylborate salts was determined over a range of ionic strengths. The equations were then used to determine  $K_{sp}$  for each species. The activity coefficient equations were confirmed by the observation that the  $K_{sp}$  was relatively constant over the range of ionic strengths. To determine the activity coefficients, the molality and ionic strength of the solutions must be calculated.

The activity coefficient equations from the OLI software for sodium, cesium, and potassium ions are valid with 'standard' salt solution up to 5 M sodium ion concentration (Figure 8). Small variations in the anion composition will not significantly impact the activity coefficient. The activity coefficient for the tetraphenylborate ion was also derived from the OLI software, based on the Siska data.<sup>4</sup> The Siska data was collected in sodium sulfate solution up to 2.0 M in sodium ion. The OLI software was used to calculate the activity coefficient to 2.0 M sodium sulfate, and then was extrapolated to 5 M sodium ion by plotting the data and fitting a curve (Figure 9). The manual curve fitting was required because the OLI software under predicted the solubility of CsTPB at 5 M sodium ion concentration. The extrapolated activity coefficient was then used as a guide and was confirmed by experiment. The TPB activity coefficient equation was confirmed by determining the KTPB and NaTPB solubilities at high ionic strength because the CsTPB solubility was difficult to measure directly. Further work is needed to verify the activity coefficient equations at intermediate ionic strength (2-4 M Na<sup>+</sup>).

Cs<sup>+</sup> activity coefficient ( $\gamma_{cs}$ ) = 0.0258 I<sub>m</sub><sup>2</sup> - 0.160 I<sub>m</sub> + 0.783

K<sup>+</sup> activity coefficient  $(\gamma_{\rm K}) = 0.0284 \ {\rm I_m}^2 - 0.219 \ {\rm I_m} + 0.777$ 

Na<sup>+</sup> activity coefficient ( $\gamma_{Na}$ ) = 0.00880 I<sub>m</sub><sup>2</sup> - 0.0701 I<sub>m</sub> + 0.701

TPB activity coeff.  $(\gamma_{TPB}) = 1.91 I_m^3 - 4.54 I_m^2 + 5.48 I_m + 0.712$ 

where the  $I_m$  is the molality-scale ionic strength of the solution.

The ionic strength of any solution is calculated from the following equation:

$$I_m = 0.5\{(Z_a^2 \times m_a) + (Z_b^2 \times m_b) + (Z_c^2 \times m_c)...\}$$

where Z is the ionic charge of the ions and m is the molal concentration (moles/1000 g solvent). For the radioactive waste

tests described in this work, the density and anion composition  $([CO_3^{-2}], [SO_4^{-2}])$  of the solutions were estimated to permit calculation of the molality. The density of salt solutions used in these experiments was determined. The following equation was fitted to the data to estimate the density (g/mL) of the salt solutions at intermediate concentrations (Figure 3).

 $\partial = 0.0452[Na^{\dagger}] + 1.006$  where  $[Na^{\dagger}]$  is the molar concentration.

The molality (m) is calculated from the molarity (M) with the following equation:

 $m = M / \{\partial - (wt. dissolved solids/1000)\}$ 

where the weight of the dissolved solids is the sum of the weight of all dissolved solids in 1 L of salt solution.

To obtain the ion solubility, the activity coefficient is then used in the solubility equilibrium equation:

 $[Cs] sol = K_{so,1} / \{ [TPB^{-}] \times (\gamma_{Cs}) \times (\gamma_{TPB}) \}$ 

where the soluble [TPB] is expressed in molarity. A similar equation is used to determine the potassium and tetraphenylborate ion solubilities.

 $K_{sp,1}$  (CsTPB) = 1.03E-10 M<sup>2</sup> at 25 °C

 $K_{sp,2}$  (KTPB) = 5.03E-8 M<sup>2</sup> at 25 °C.

 $K_{sp.3}$  (NaTPB) = 0.62 M<sup>2</sup> at 25 °C.

For comparison of the OLI-derived equations to experimental results, the NaTPB solubility was determined in salt solution (Table 5). The sodium concentration in Table 5 is the final value including the contribution from salt solution and dissolved NaTPB. The NaTPB equilibrium constant  $(K_{sp,3})$  was estimated to be 0.62, and the TPB activity coefficient was calculated. The sodium activity coefficient was calculated using the equation above. The value for  $K_{so,3}$  (0.62) was selected, rather than the average value, because the sodium activity coefficient was based on a model of the salt solution and is only valid for low concentrations of NaTPB. At high concentration of NaTPB, the equation for the sodium activity may vary. This is not a concern for ITP operations because the condition with high concentration of NaTPB (>0.1 M) is not encountered. The results indicate good agreement between the OLI data and the experimental results (Figure 10). The density of the NaTPB-saturated salt solution was also determined (Figure 11).

Total [Na] (M)	<u>[TPB] (M)</u>	<u>Density (g/mL)</u>	<u>Ksp3 (NaTPB)</u>
4.23	0.0016	1.179	0.622
2.39	0.043	1.091	0.875
1.05	0.111	1.060	0.299
0.633	0.163	1.056	0.237
0.473	0.332	1.036	0.381
		av	$erade \cdot 0.48$

#### Table 5. NaTPB Solubility in Salt Solution

#### Temperature Dependence

The temperature dependence of the solubility product constants was derived for CsTPB and KTPB. The dependence of the KTPB solubility with temperature agrees with that of Siska<sup>4</sup> (Figure 12). The variance of CsTPB solubility with temperature nearly parallels the Siska data, but is offset by the difference in solubility (Figure 13). The NaTPB solubility data (Figure 14) agrees with earlier results<sup>6</sup> indicating only slight dependence of solubility with temperature. Equations for the equilibrium constants were derived from the experimental data and are valid from 25 to 65 °C:

 $K_{sp,1}$  (CsTPB) = 2.328E-11e<sup>(5.199E-2T)</sup>

 $K_{sp,2}$  (KTPB) = 7.81E-9 e<sup>(6.30E-2T)</sup>

 $K_{sp,3}$  (NaTPB) = 0.439  $e^{(1.39E-2T)}$ 

The values for  $K_{sp,1}$  and  $K_{sp,2}$  were derived from a series of experiments over a range of concentration of salt solution. The data are more erratic at high temperature than at ambient temperature (i.e.,  $K_{sp}$  is more variable throughout the range of ionic strengths). This larger variance is probably due to experimental variability during handling due to additional dilutions. The average values for  $K_{sp,1}$  and  $K_{sp,2}$ , and the standard deviation were calculated. Additional data for KTPB, CsTPB, and NaTPB at elevated temperatures are shown in Table 8.

Table	6.	Calculation	of	K.,	and	K., ,	vs.	[Na <sup>+</sup> ]	at	25	°C
											_

[Na+]	(M)	CSTPB KSp1 (M <sup>2</sup> )	KTPB Ksp2 (M <sup>2</sup> )
1.41		1.06E-10	5.35E-8
0.47		1.51E-10	8.35E-8
0.14		9.65E-11	3.81E-8
0.047		5.86E-11	2.59E-8
	average:	1.03E-10	5.03E-8
	std. dev.	3.80E-11	2.49E-8

[Na+]	(M)	CsTPB Ksp1 (M <sup>2</sup> )	KTPB Ksp2 (M <sup>2</sup> )
4.7		4.59E-10	1.78E-6
1.41		1.49E-9	3.63E-7
0.47		1.70E-9	5.03E-7
0.14		8.27E-10	3.04E-7
0.047		1.96E-10	1.75E-7
	average:	9.34E-10	6.26E-7
	std. dev.:	6.47E-10	6.58E-7

Table 7. Calculation of  $K_{sp,1}$  and  $K_{sp,2}$  vs. [Na<sup>+</sup>] at 65 °C

Table 8. Calculation of K<sub>sp.</sub> at Elevated Temperatures

	T (°C)	[Na+] (M)	$Ksp (M^2)$
KTPB	50	0.47	7.52E-8
CsTPB	50	0.47	1.90E-10
NaTPB	65	2.388	1.08

#### Effect of Organics, Anions, and Potassium

The impact of organics, K:Cs ratio, and the composition of the anions was also determined (Table 9). The organics test utilized a 0.25 M [Na+] standard alkaline salt solution simulant and 1000 mg/L each of benzene, phenol, and phenylboric acid. The composition of the anions was varied using a high hydroxide formulation substituting sodium hydroxide for the sodium sulfate and carbonate (Table 2). The results indicate that the impact of the organic and anionic components is minimal.

Table 9. Impact of Organics, Anions, and Potassium

Experiment	CsTPB Ksp1 (M <sup>2</sup> )	KTPB Ksp2 (M <sup>2</sup> )
organics	1.13E-10	4.92E-8
high hydroxide	1.32E-10	5.02E-8

For comparison to Siska's<sup>4</sup> experimental data, the activity coefficient equations determined using the OLI software were used to calculate the  $K_{sp,1}$  (CsTPB) and  $K_{sp,2}$  (KTPB) values (Table 10). The Siska data was collected in sodium sulfate solutions and the OLI software generated the activity coefficients based on ionic strength. This approach is self-consistent because the activity coefficients generated by the OLI program were derived from the the Siska data. This exercise demonstrates that the software and derived equations are consistent with the original data.

[Na+]	(M)	CsTPB Ksp1 (M <sup>2</sup> )	KTPB <u>Ksp2 (M<sup>2</sup>)</u>
2.0		1.36E-9	2.77E-8
0.7		9.64E-10	2.55E-8
0.3		1.19E-9	2.80E-8
0.05		8.84E-10	1.91E-8
	average:	1.10E-9	2.51E-8
	std. dev.	2.29E-10	4.14E-9

Table 10. Calculation of  $K_{sp,1}$  and  $K_{sp,2}$  from Siska's Data

The average equilibrium constant for CsTPB from the Siska report<sup>4</sup> is an order of magnitude higher than that observed in the current work  $(1.03E-10 \text{ M}^2)$ . The KTPB equilibrium constant determined in this study  $(5.03E-8 \text{ M}^2)$  is similar to that observed by Siska.

To examine the discrepancy between the two studies, two experiments were performed using 0.124 M sodium sulfate solution (0.25 M [Na<sup>+</sup>]) and a mixture of potassium and cesium ions (Table 11). Two ratios of TPB<sup>-</sup> to potassium were used to examine the impact of increased TPB<sup>-</sup> on the equilibrium condition. The CsTPB and KTPB equilibrium constants were determined (Table 11) and are nearly identical with those determined using salt solution (K<sub>sp,1</sub> =  $1.03E-10 \text{ M}^2$ ; K<sub>sp,2</sub> =  $5.03E-8 \text{ M}^2$ ). The results suggest that the mixture of potassium and cesium ions may have an impact on the observed solubility of cesium, or that the Siska data or the activity coefficient are in error.

#### Table 11. $K_{sp,1}$ and $K_{sp,2}$ in Aqueous Sodium Sulfate

TPB:K	CsTPB Ksp1 (M <sup>2</sup> )	KTPB Ksp2 (M <sup>2</sup> )
1.25:1	1.43E-10	3.92E-8
1:1	1.77E-10	4.39E-8

An additional experiment, using 0.125 M sodium sulfate solution with no added potassium, verifies the conclusion that the ratio of potassium to cesium influences the solubility. The resulting  $K_{sp,1}$ = 3.54E-9 M<sup>2</sup> is even higher than the Siska data (1.10E-9 M<sup>2</sup>) in pure sodium sulfate. The large excess of TPB<sup>-</sup> did not impact the equilibrium constants (Table 11), indicating that the reason for the discrepancy is not related to the presence of excess TPB<sup>-</sup>. The system is well behaved and the data suggests that additional anionic TPB<sup>-</sup> only causes a shift in the equilibrium (Equation 1). Furthermore, previous equations that were used for calculating the solubility of CsTPB in salt solutions<sup>3</sup> did not factor in the ionic strength but only described the solubility in terms of the molarity of sodium. Both the ionic strength and the potassium-tocesium ratio appear important to the Cs<sup>+</sup> solubility. More research into the influence of the ratio of potassium and cesium is needed to better predict the CsTPB solubility in solutions that contain high concentrations of potassium.

#### Comparison to Radioactive Waste

Using the equations derived from the current work, the predicted cesium solubility can be compared with the observed solubility during the precipitate washing cycle of the 1983 In-Tank Demonstration.<sup>7</sup> It was assumed for these calculations that the Cs-137 is 35 atom % of the total cesium present (Table 12). The measured concentration of TPB<sup>-</sup> was used for all calculations.

## Table 12. Calculated vs. Observed Cs Radioactivity for 1983 In-Tank Demonstration

$\underline{[Na^+](M)}$	[TPB <sup>-</sup> ]	calculated Cs	<u>observed Cs</u>
5.1	0.0016 M	1.0 (nCi/g)	2.0 (nCi/g)
1.2	0.067	2.1	2.4
0.57	. 0.025	8.5	7.3
0.17	0.0088	43.5	28.0

Similarly, the cesium solubility during sampling and recent experiments using Tank 48H slurry (Table 13) can be compared.<sup>8</sup> The sample from Tank 48H on December 28 (Table 13) is assumed to contain no remaining soluble (sodium) tetraphenylborate. To calculate the solubility of cesium, the solubility of KTPB was assumed to be the only source of soluble tetraphenylborate ion.

### Table 13. Calculated vs. Observed Cs Radioactivity for PVT-1 Samples and Testing

			Cesium	(nCi/g)
<pre>exp't/sample</pre>	<u>[Na<sup>+</sup>](M)</u>	[TPB-] (M)	calculated	observed
Experiment (#4A) <sup>8</sup>	3.5	2.9E-4	28.2	11.7
Experiment (#2) <sup>8</sup>	3.83	2.0E-4	28.4	269
Tk 48H, 12/28/95	4.70	2.3E-5*	102	28

\*estimated concentration

The calculated cesium activities agree reasonably well with the observed cesium activity for the 1983 In-Tank Demonstration (Table 12). In Table 13, the two samples from PVT-1 testing are not self-consistent. This discrepancy suggests that the experiments were not at equilibrium or that the tetraphenylborate analysis is in error. It is likely that the PVT-1 test solutions were not at equilibrium due to the short mixing time (<2 hours). Considering the approximation of tetraphenylborate concentration in this estimate, the analysis results agree reasonably well with the predicted value.

#### <u>Conclusions</u>

Initial experiments to quantify the NaTPB excess required to achieve decontamination at ITP are complete. The cesium in these solutions was often below the detection limit of the instrument. The activity coefficient of tetraphenylborate ion at high ionic strength was verified by determining the sodium tetraphenylborate solubility. The system seems well behaved, and is not effected by organic compounds. The effect of anions can be mathematically compensated by using the ionic strength instead of the molar concentration of species in calculations.

The rate of precipitation can be slow, but appears to be complete within 160 hours at ambient temperature. Further testing to quantify the rate of precipitation with excess NaTPB is needed.

The equations and equilibrium constants derived from this work represent the best available data with salt solutions simulating the ITP process.

Further work is needed in the following areas:

- Evaluate the potassium to cesium ratio to better define the impact on both the equilibrium constant and on the rate of precipitation
- Examine the precipitation kinetics with excess TPB<sup>-</sup> to further quantify the time required for mixing in Tank 48H
  - Examine the mixing and addition rates on the rate of precipitation

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### **Ouality Assurance**

The experimental methods and results were recorded in laboratory notebooks

#### <u>Acknowledgements</u>

Analytical analyses were performed by Melton Bryant. These nonroutine analyses required considerable effort. Steve Serkiz provided assistance in developing the activity coefficient equations.

#### Attachment

Analytical data analyses (7 pages)

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Distribution: H.H. Elder, 704-S J.T. Carter, 704-25S L.M. Papouchado, 773-A G.T. Wright, 773-A B.L. Lewis, 703-H M.C. Chandler, 703-H N.F. Chapman, 512-11S L.O. Dworjanyn, 779-2A J.E. Marra, 704-56H A.W. Wiggins, 241-152H D.D. Walker, 773-A C.A. Nash, 773-43A W.L. Tamosaitis, 773-A R.A. Peterson, 676-T M.S. Miller, 704-72S C.L. Crawford, 773-41A W.R. Parish, 703-H IWT File, 773-A

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\*



1

Density of standard salt solution

Density = 4.522E-2\*[Na+] + 1.006E+0

18

Figure 3. Density of Salt Solution





WSRC-TR-96-0384



Figure 5. Near-stoichiometric STPB addition at 4.7 M [Na+] Kinetics Test at 25 C

\*

20

K (ppm)



\*

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Kinetics Test at 25 Figure 7. Stoichiometric STPB Addition at 1.41 M [Na+] C



Figure 8. Cesium and Potassium Activity Coefficients vs. Ionic Strength

where Im = the molality scale ionic strength







Figure 10. Comparison of Activity Coefficient Calculated from OLI 25 °C) Software vs. STPB Solubility (T =



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÷





f CSTPB
ependence of
Temperature I
13.
Figure

(CSTPB)

Siska Kl

(CSTPB)

■ K1



(Siska data) Kspl = 1.974E-10 \* exp( 6.971E-2\*T

(SRTC data) Kspl = 2.328E-11 \* exp( 5.199E-2\*T )

Figure 14. Temperature Dependence of STPB



f(x) = 4.39E-1 + exp(1.39E-2+x)

■ K3

Kitkeise	_										·····				
KNI-12  KNI-52  KNI-54  KNI-54<	Kinet	cs test blanks										·			
B  200  T00  780  570  297  Constraints  Constraints <thconstraints< td="" th<=""><td></td><td>KIN-b-1</td><td>KIN-b-2</td><td>KIN-b-3</td><td>KIN-b-4</td><td>Avg. Init. ppb</td><td>Std. dev.</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></thconstraints<>		KIN-b-1	KIN-b-2	KIN-b-3	KIN-b-4	Avg. Init. ppb	Std. dev.								
K  32000  33000  332667  577  Local  Local <thlocal< th="">  Local  Local</thlocal<>	В	230		700	780	570	297								
1700  1800  1800  1700  1900  CLl-derive-I activity coeff. from Siste data  Sector Siste	к	32000		33000	33000	32667	577	1							-
Kinel set  Kinel (Kin-24)  Ang_ mit, pp. Sid. dev.  Na (M)  on. Strong M  Ga accost  K act, cost  TPB act, cost  K    8  2800  4100  3200  3033  208  2.28E-04  0.28  0.3  0.7372  0.7142  2.00  3.94E-08    6  38  44  37  40  4  2.98E-07  0.8  0.3  0.7372  0.7142  2.00  3.94E-08    Kin-172  Kin-572  Kin-372  Ang_ mit, pb, Sid. dev.  Na (M)  0.7372  0.7142  2.00  4.06E-10    Kin-172  Kin-572  Kin-572  Ang, mit, pb, Sid. dev.  Na (M)  0.3  0.7372  0.7142  2.00  4.06E-08    Kin-172  Kin-524  Kin-524  1.28E-04  0.28  0.3  0.7372  0.7142  2.00  4.06E-04    Kin-174  Kin-524  Kin-524  1.28E-04  0.28  0.3  0.7372  0.7142  2.00  5.00  5.000  1.00E-04  0.28  0.3  0.7372	Cs	1700		1600	1800	1700	100		OLI-de	erive	d activity	coeff. from	Siska data	a	
KINI-124  KINI-324  KINI-324  Kuni, ppb Std, dev.  Molently  Na (M)  Ion. Strength  Care accoeff  TP Bet. coeff  X    K  5000  4600  4733  2201  1.21E-04  0.3  0.7372  0.7142  2.00  3.04E-08    Konetics test  44  9.7  400  4  2.98E-07   K  1.00E-10  1.00E-10  1.00E-10  1.00E-10  1.00E-10  1.00E-10   K  1.00E-10	Kineti	cs test										·			
9  2800  3100  3200  4203  200  228E-04  0.28  0.3  0.7372  0.7142  2.00    Ca  38  44  37  40  4  2.98E-07		KIN-1-24	KIN-2-24	KIN-3-24	Avg. Init. ppb	Std. dev.		Molarity	Na (M)		Ion. Strength	Cs act. coeff	K act. coeff.	TPB act. coeff.	К
K  5000  4600  4733  221  1.21E-04	в	2800	3100	3200	3033	208		2.28E-04		0.28	0.3	0.7372	0.7142	2.00	
On  36  44  37  40  4  2.98E-07  Na (M)	K	5000	4600	4600	4733	231		1.21E-04							3.94E-08
Totolica test  Market	Ca	38	44	37	40	4		2.98E-07							1.00E-10
KIN-172  KIN-572  KIN-572 <t< td=""><td>Kineti</td><td>cs test</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></t<>	Kineti	cs test													
B  1 1 2 200  1 2 200  1 1 2 24E-04  0.28  0.3  0.7372  0.7142  2.00    K  4 600  4 900  4 750  2 12  1 21E-04  0.28  0.3  0.7372  0.7142  2.00    Kinetics test   3 2  3 9  3 6  5  2.67E-07   9.21E-11    Kinv1-144  KiN-144  KiN-3-144  Avg. Init.ppb  Sid. dev.  Na (M)   Kinv1-144  Kinv2-144  Kinv2-1		KIN-1-72	KIN-2-72	KIN-3-72	Ava, Init, pob	Std. dev.			Na (M)						K
K  4600  4750  212  121E-04  000	B	3200	3000		3100	141	<u> </u>	2.34E-04		0.28	0.3	0.7372	0.7142	2.00	
Ch  32  39  36  5  1.07E-07  Na (M)  Aug. Init. ppb  Std. dev.  Na (M)  KIN-1:44  KIN-2:144  KIN-3:144  Aug. Init. ppb  Std. dev.  Na (M)  KIN-1:44  KIN-2:144  KIN-3:144  Aug. Init. ppb  Std. dev.  Na (M)  KIN-1:44  KIN-2:16  KIN-2:17  KIN-2:18  KIN-2:18  KIN-2:18<	K	4600	4900		4750	212		1 21E-04		0.20					4.06E-08
OB  OB <thob< th="">  OB  OB  OB<!--</td--><td></td><td>32</td><td>30</td><td></td><td>36</td><td>5</td><td><u> </u></td><td>2 67E-07</td><td></td><td></td><td></td><td></td><td></td><td></td><td>9 21 F-11</td></thob<>		32	30		36	5	<u> </u>	2 67E-07							9 21 F-11
Kink-1:44  Kink-1:44 <t< td=""><td>Kinoti</td><td>ce test</td><td>00</td><td></td><td></td><td> <b>-</b></td><td>†</td><td>2.07 -07</td><td></td><td></td><td></td><td></td><td>· · · ·</td><td></td><td>0.212 11</td></t<>	Kinoti	ce test	00			<b>-</b>	†	2.07 -07					· · · ·		0.212 11
Numerical  Numerical <t< td=""><td>INHIGU</td><td>KINL1_1AA</td><td>KIN 2 144</td><td>KIN-2-144</td><td>Ava init pob</td><td>Std. dov</td><td>1</td><td></td><td>No /M</td><td></td><td></td><td></td><td>·</td><td></td><td>K</td></t<>	INHIGU	KINL1_1AA	KIN 2 144	KIN-2-144	Ava init pob	Std. dov	1		No /M				·		K
b  2500  2500  2500  2500  100  2500  100  2500  100  2500  100  2500  100  2500  100  2500  100  2500  100  2500  2600  277.76  217.76  217.76  217.76  217.76  217.76  217.76  217.76  217.76  217.76  217.76  217.76 <td>-</td> <td>2900</td> <td>2900</td> <td>2100</td> <td>2000</td> <td>172</td> <td></td> <td>2 165-04</td> <td>ive (ivi)</td> <td>0.28</td> <td>0.3</td> <td>0 7372</td> <td>0 7142</td> <td>2.00</td> <td><u></u></td>	-	2900	2900	2100	2000	172		2 165-04	ive (ivi)	0.28	0.3	0 7372	0 7142	2.00	<u></u>
A  3500  5000  4100  4260  0.24  1.128201  0.00200  0.00200  0.00200    Kihelco steat  *  45  45  48  46  2  3.48E-07  1.10E-10    Kihelco steat  *  . </td <td></td> <td>5000</td> <td>2000</td> <td>4100</td> <td>2900</td> <td>624</td> <td></td> <td>1 22 04</td> <td></td> <td>0.20</td> <td>0.0</td> <td>0.7572</td> <td>0.7.142</td> <td>2.00</td> <td>3 795-09</td>		5000	2000	4100	2900	624		1 22 04		0.20	0.0	0.7572	0.7.142	2.00	3 795-09
Ga  43  44<	<u> </u>	5300	5000	4100	4000	024		2 465 07					<u> </u>		1 105-10
Kirkeize Istill  Kirk-216  Kirk-3216  Kirk-3216  Aug. Init. ppb  Std. dev.  Na (M)  K  K    B  2000  2800  3100  2933  153  2.19E-04  0.28  0.3  0.7372  0.7142  2.00    Aster-08  61  69  74  68  7  5.12E-07  1.85E-10  1.85E-10    Washing/dilution test  W/D-1-1  W/D-1-2  W/D-1-3  Avg. final ppb  Std. dev.  Na (M)  Cs act. coeff  K act. coeff.  TPB act. coeff    W/D-1-BLK  W/D-1-1  W/D-1-2  W/D-1-3  Avg. final ppb  Std. dev.  Na (M)  Cs act. coeff  K act. coeff.  TPB act. coeff.  K    B  2100  560  540  520  220  rot at equilibrium  #VALUE!  #VALUE! <t< td=""><td>16-11</td><td>45</td><td>40</td><td>+0</td><td>40</td><td> č</td><td>i</td><td>3.40E-07</td><td></td><td></td><td></td><td></td><td></td><td></td><td>1.102-10</td></t<>	16-11	45	40	+0	40	č	i	3.40E-07							1.102-10
NRV-1216  NRV-2216  NRV-2217  NRV-2216  NRV-2217  NRV-2217  NRV-2217  NRV-2217  NRV-2217  NRV-2217  NRV-2216  NRV-2217  NRV-2216  NRV-2217  NRV-2216  NRV-2217  NRV-2216  NRV-2217	Kineti				Arra tala mula	0.4 4									V
B  2000  2000  3100  2933  153  2.192-04  0.28  0.3  0.7372  0.7142  2.00    Ca  610  5600  5600  5600  5467  321  1.40E-04  1.65E-10  1.65E-10    Washing/dlution test  W/D-1-1  W/D-1-2  W/D-1-3  Avg. final ppb  Std. dev.  Na (M)  Cs act. coeff  K act. coeff.  TPB act. coeff. K    B  2100  560  540  520  540  20  Na (M)  Cs act. coeff  K act. coeff.  TPB act. coeff. K    B  2100  660  540  520  540  20  Na (M)  Cs act. coeff  K act. coeff. K    B  2100  660  540  520  540  20  Na (M)  Cs act. coeff  K act. coeff. K    WD-2-2  W/D-2-1  W/D-2-2  W/D-2-3  Avg. final ppb  Sid. dev.  Na (M)  Cs act. coeff  K act. coeff. K    Washing/dlution test  VD-2-2  W/D-2-3  Avg. final ppb  Sid.	<u> </u>	KIN-1-216	KIN-2-216	KIN-3-210	Avg. Init. ppo	SIG. Gev.	}	0.105.04	INAL (M)	0.00	0.0	0 7070	0 71 40	0.00	<u>n</u>
K  5/00  5800  5867  321  1.402-04  4.302-06    Washing/dilution test  5.12E-07  5.12E-07  1.65E-10    W/D-1-8LK  W/D-1-1  W/D-1-2  W/D-1-2  W/D-1-3  Avg. final ppb  Std. dev.  Na (M)  Cs act. coeff  TPB act. coeff  K    B  2100  560  540  520  540  20  ?????????  4.7  5.55  0.6896  0.4419  21.7.76    K  560000  110000  98000  30000  79333  43143 not at equilibrium  Cs act. coeff  K  #VALUEI    Washing/dilution test  ////////////////////////////////////	B	2900	2800	3100	2933	153	<u> </u>	2.192-04		0.28	0.3	0.7372	0./142	2.00	4 005 00
Ca  61  69  74  68  7  5.12E-07  1.55E-10    Washing/dilution test      Na (M)  Ca act. coeff  K act. coeff  TPB act. coeff (K    B  2100  560  540  520  540  201 ????????  4.7  5.55  0.6896  0.4419  217.76    K  560000  110000  98000  30000  79833  43143 not at equilibrium   #VALUEI    K  560000  670  520  220  470  229 not at equilibrium   #VALUEI    Washing/dilution test        #VALUEI    W/D-2-1  W/D-2-2  W/D-2-2  W/D-3-1  Avg. final ppb  Std. dev.      5.35E-08    Ca  10000  4900  4700  4330  4633  306  1.19E-04       5.35E-08    Ca  10000  26	K	5700	5100	5600	546/	321	<u> </u>	1.402-04							4.302-08
Washing/dilution test  W/D-1-1  W/D-1-2  W/D-1-3  Avg. final ppb  Std. dev.  Na (M)  Cs act. coeff  K act. coeff.  TPB act. coeff.    B  2100  560  540  520  540  20  ????????  4.7  5.55  0.6896  0.4419  217.76    K  560000  110000  98000  30000  79333  43143 not at equilibrium   #VALUEI    K  560000  11000  98000  30000  79333  43143 not at equilibrium   #VALUEI    Washing/dilution test      #VALUEI    W/D-2-1  W/D-2-2  W/D-2-3  Avg. final ppb  Std. dev.       B  180  1500  2100  280  4633  306  1.19E-04     5.35E-08    K  170000  4900  4700  4300  4633  306  1.19E-04    5.35E-08    5.35E-08	Cs	61	69	74	68	7		5.12E-07							1,65E-10
W/D-1-BLK  W/D-1-1  W/D-1-3  Avg. final ppb Std. dev.  Na (M)  Cs act. coeff.  TPB act. coeff.  TPB act. coeff.    K  560000  110000  98000  30000  78333  43143 not at equilibrium  5.55  0.6896  0.4419  21.7.76    K  560000  110000  980000  30000  78333  43143 not at equilibrium  4.7  5.55  0.6896  0.4419  21.7.76    Ca  31000  670  520  220  470  229 not at equilibrium  4.7  5.55  0.6896  0.4419  21.7.76    Washing/dilution test  W/D-2-1  W/D-2-2  W/D-2-3  Avg. final ppb Std. dev.  4.7  1.55  0.5086  5.37    K  170000  4900  4700  4300  4633  306  1.19E-04  5.35E-08  5.35E-08    Ca  10000  400  20  27  12  2.01E-07  1.06E-10  1.06E-10    W/D-3-ELK  W/D-3-1  W/D-3-2  W/D-3-3  Avg. final ppb	Wash	ing/dilution tes													
B  2100  560  540  520  540  2017777777  4.7  5.55  0.6896  0.4419  217.76    K  560000  110000  98000  30000  79333  43143  not at equilibrium  ////////////////////////////////////	L	W/D-1-BLK	W/D-1-1	W/D-1-2	W/D-1-3	Avg. final ppb	Std. dev.		Na (M)			Cs act. coeff	K act. coeff.	TPB act. coeff.	ĸ
K  560000  110000  98000  30000  79333  43143 not at equilibrium  Available  #VALUEI    Ca  31000  670  520  220  470  229 not at equilibrium  #VALUEI    W/D-2-BLK  W/D-2-1  W/D-2-2  W/D-2-3  Avg. final ppb  Std. dev.  #VALUEI    B  180  1500  2100  2300  1967  416  1.65E-04  1.41  1.54  0.5977  0.5086  5.37    K  170000  400  4700  4300  4633  306  1.19E-04      5.35E-08    Ca  10000  40  20  20  27  12  2.01E-07	В	2100	560	540	520	540	20	77777777		4.7	5.55	0.6896	0.4419	217.76	
Cs  31000  670  520  220  470  229 not at equilibrium  Image: Constant equilibrium  MV/LUE!    Washing/dilution test  W/D-2-1  W/D-2-2  W/D-2-3  Avg. final ppb  Sid. dev.  Image: Constant equilibrium  Image: Constant equ	ĸ	560000	110000	98000	30000	79333	43143	not at equilibri	um						#VALUE!
Washing/dilution test  w/D-2-3  Avg. final ppb  Std. dev.  w/D-2  w/D-2  w/D-2-3  w/D-2-3  Avg. final ppb  Std. dev.  w/D-2  w/D-2  w/D-2  w/D-2-3  Avg. final ppb  Std. dev.  w/D-2  w/D-2  w/D-2  w/D-2-3  Avg. final ppb  Std. dev.  w/D-2  w/D-2  w/D-2  w/D-2-3  Avg. final ppb  Std. dev.  w/D-2  w/D-3  Ref final ppb  Std. dev.  w/D-3  w/D-3  Ref final ppb  Std. dev.  w/D-3  w/D-3  W/D-3  Ref final ppb  Std. dev.  w/D-3  w/D-3  W/D-3  Ref final ppb  Std. dev.  w/D-3  Ref f	Ca	31000	670	520	220	470	229	not at equilibri	um						#VALUE!
W/D-2-BLK  W/D-2-1  W/D-2-2  W/D-2-3  Avg. final ppb  Std. dev.  Image: Constraint of the state of the stat	Wash	ing/dilution test													
B  180  1500  2100  2300  1967  416  1.65E-04  1.41  1.54  0.5977  0.5086  5.37    K  170000  4900  4700  4300  4633  306  1.19E-04   5.35E-08    Cs  10000  40  20  20  27  12  2.01E-07      5.35E-08    WD-3-BLK  W/D-3-1  W/D-3-2  W/D-3-3  Avg. final ppb  Std. dev.        B  <100  280  260  420  320  87  2.40E-05  0.47  0.5  0.7094  0.6751  2.56    K  260000  81000  76000  79000  78667  2517  2.01E-03    8.35E-08    K  260000  81000  76000  79000  78667  2517  2.01E-03      8.35E-08		W/D-2-BLK	W/D-2-1	W/D-2-2	W/D-2-3	Avg. final ppb	Std. dev.								
K  170000  4900  4700  4300  4633  306  1.19E-04   5.35E-08    Cs  10000  40  20  20  27  12  2.01E-07    1.06E-10    Washing/dilution test  W/D-3-BLK  W/D-3-2  W/D-3-3  Avg. final ppb  Std. dev.	В	180	. 1500	2100	2300	1967	416	1.65E-04		1.41	1.54	0.5977	0.5086	5.37	
C8  10000  40  20  20  27  12  2.01E-07    1.06E-10    Washing/dilution test          1.06E-10    W/D-3-BLK  W/D-3-1  W/D-3-2  W/D-3-3  Avg. final ppb  Std. dev. <t< td=""><td>К</td><td>170000</td><td>4900</td><td>4700</td><td>4300</td><td>4633</td><td>306</td><td>1.19E-04</td><td></td><td></td><td>1</td><td></td><td></td><td></td><td>5.35E-08</td></t<>	К	170000	4900	4700	4300	4633	306	1.19E-04			1				5.35E-08
Washing/dilution test  Image: Minimized marked	Cs	10000	40	20	20	27	12	2.01E-07							1.06E-10
W/D-3-BLK  W/D-3-1  W/D-3-2  W/D-3-3  Avg. final ppb  Std. dev.	Wash	ing/dilution test													
B  <100  280  260  420  320  87  2.40E-05  0.47  0.5  0.7094  0.6751  2.56    K  260000  81000  76000  79000  78667  2517  2.01E-03    6.35E-08    Ca  9700  410  460  510  460  50  3.46E-06      8.35E-08    Washing/dilution test		W/D-3-BLK	W/D-3-1	W/D-3-2	W/D-3-3	Avg. final ppb	Std. dev.								
K  260000  81000  76000  79000  78667  2517  2.01E-03    8.35E-08    Cs  9700  410  460  510  460  50  3.46E-06 <td>B</td> <td>&lt;100</td> <td>280</td> <td>260</td> <td>420</td> <td>320</td> <td>87</td> <td>2.40E-05</td> <td></td> <td>0.47</td> <td>0.5</td> <td>0.7094</td> <td>0.6751</td> <td>2.56</td> <td></td>	B	<100	280	260	420	320	87	2.40E-05		0.47	0.5	0.7094	0.6751	2.56	
Cs  9700  410  460  510  460  50  3.46E-06    1.51E-10    Washing/dilution test <td>ĸ</td> <td>260000</td> <td>81000</td> <td>76000</td> <td>79000</td> <td>78667</td> <td>2517</td> <td>2.01E-03</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>8.35E-08</td>	ĸ	260000	81000	76000	79000	78667	2517	2.01E-03							8.35E-08
Washing/dilution test  Image: Window Sector	Cs	9700	410	460	510	460	50	3.46E-06							1.51E-10
W/D-4-BLK  W/D-4-1  W/D-4-2  W/D-4-3  Avg. final ppb  Std. dev.  Image: Constraint of the state of the stat	Wash	ing/dilution test													
B  <100  260  270  280  270  10  2.33E-05  0.14  0.15  0.7595  0.7449  1.44    K  170000  59000  59000  61000  59667  1155  1.53E-03  3.81E-08  3.81E-08    Cs  8200  470  520  503  29  3.79E-06  9.65E-11    Washing/dilution test  V/D-5-1  W/D-5-2  W/D-5-3  Avg. final ppb  Std. dev.  V    B<  <100		W/D-4-BLK	W/D-4-1	W/D-4-2	W/D-4-3	Avg. final ppb	Std. dev.								
K  170000  59000  59000  61000  59667  1155  1.53E-03	в	<100	260	270	280	270	10	2.33E-05		0.14	0.15	0.7595	0.7449	1.44	
Cs  8200  470  520  520  503  29  3.79E-06  9.65E-11    Washing/dilution test  ////////////////////////////////////	K	170000	59000	59000	61000	59667	1155	1.53E-03							3.81E-08
Washing/dilution test  United by the second sec	Cs	8200	470	520	520	503	29	3.79E-06							9.65E-11
W/D-5-BLK  W/D-5-1  W/D-5-2  W/D-5-3  Avg. final ppb  Std. dev.  0 <th0< td=""><td>Wash</td><td>ing/dilution test</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>· · · · · · · · · · · · · · ·</td><td></td><td></td><td></td><td></td></th0<>	Wash	ing/dilution test									· · · · · · · · · · · · · · ·				
B <100 270 260 210 247 32 2.23E-05 0.047 0.05 0.7750 0.7662 0.98		W/D-5-BLK	W/D-5-1	W/D-5-2	W/D-5-3	Avo, final poh	Std. dev.								
	в	<100	270	260	210	247	32	2,23E-05		0.047	0.05	0.7750	0.7662	0.98	

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к	179000	58000	57000	68000	61000	6083	1.56E-03						2.59E-08
Cs	7300	440	490	460	463	25	3.49E-06						5.86E-11
Sodiu	ım sulfate (0.12	5 M) test with	potassium										
	Sulf Ion BLK	Sulf Ion -1	Sulf Ion - 2	Sulf Ion - 3	Avg. final ppb	Std. dev.							
В	<100	1800	1800	1800	1800	0	1.66E-04	0.25	0.38	0.7258	0.6983	2.24	
К	26000	5600	6100	5900	5867	252	1.50E-04						3.92E-08
Cs	2000	80	80	50	70	17	5.27E-07						1.43E-10
				1									
Stand	lard salt solution	n test											
	SS-blank	SS-1	SS-2	SS-3	Avg. final ppb	Std. dev.							
В	540	1700	1900	2100	1900	200	1.26E-04	0.25	0.29	0.7387	0.7162	1.97	
К	27000	5000	3300	3900	4067	862	1.04E-04						1.84E-08
Cs	1800	60	50	50	53	6	4.01E-07						7.33E-11
	orig. Cs anal.	580	490	510									
Stand	ard salt solution	n, no potassiun	test										
	SSOK-BLK	SSOK-1	SS0K-2	SS0K-3	Avg. final ppb	Std. dev.							
в	<10	1700	1800	1800	1767	58	1.62E-04	0.25	0.29	0.7387	0.7162	1.97	
К	2600	520	860	1560	980	530	2.51E-05						5.74E-09
Cs	1500	940	1100	980	11300	1572	8.50E-05						2.01E-08
	orig. Cs anal.	9900	13000	11000									
Exces	s TPB Washing	dilution test											
	E-W/D1-BLK	E-W/D-1-1	E-W/D-1-2	E-W/D-1-3	Avg. final pob	Std. dev.							
В	2800	3100	2700	2200	2667	451	2.46E-04	4.7	5.55	0.6896	0 4419	217 76	
K	590000	520000	520000	510000	516667	5774	1.32E-02		0.00		0.1110		3 12E-04
Ċs	29000	15000	18000	18000	17000	1732	1.28E-04						4 72E-06
Exces	s TPB Washing	dilution test		1			11202 01						4.722-00
	E-W/D2-BLK	E-W/D-2-1	E-W/D-2-2	E-W/D-2-3	Ava, final pob	Std. dev.							
В	650	11000	12000	12000	11667	577	1.02E-03	1.41	1.54	0.5977	0.5086	5 37	
ĸ	182000	4800	4500	5500	4933	513	1.26E-04			0.0077	0.0000	0.07	3 51E-07
Cs	8300	<20	<20	<20	#DIV/01	#DIV/01	#DIV/01			· · · ·			#DIV/01
Exces	s TPB Washing	dilution test											
	E-W/D3-BLK	E-W/D-3-1	E-W/D-3-2	E-W/D-3-3	Ava, final pob	Std. dev.							
В	680	7600	7200	11000	8600	2088	7.33E-04	0.47	0.5	0 7094	0.6751	2.56	
ĸ	200000	4000	4800	4800	4533	462	1.16E-04				0.0.01		1 47E-07
Cas	8700	<20	<20	<20	#DIV/01	#DIV/01	#DIV/01						#DIV/01
Exces	s TPB Washing	dilution test											
	E-W/D4-BLK	E-W/D-4-1	E-W/D-4-2	E-W/D-4-3	Avg. final ppb	Std. dev.							
В	<100	6100	6800	6800	6567	404	6.06E-04	0.14	0.15	0.7595	0.7449	1.44	
К	140000	1900	580	1600	1360	692	3.48E-05						2.26E-08
Cs	7000	<20	<20	<20	#DIV/01	#DIV/01	#DIV/01						#DIV/01
Exces	s TPB Washing	dilution test		······································				• • • • • • • • • •					
	E-W/D5-BLK	E-W/D-5-1	E-W/D-5-2	E-W/D-5-3	Avg. final pob	Std. dev							
В	7800	8400	8200	9000	8533	416	6.78E-05	0 047	0.05	0 7750	0 7662	0.08	
K	120000	850	<100	<100	850	#DIV/01	2 17E-05	0.047	0.00	0.1700	0.7002	0.30	1 10F-00
Cs	0069	<20	<20	<20	#DIV/01	#DIV/01	#DIV/01			······			#DIV/01
Organ	ic salt impact to	est											
	ORG-4-BLK	OBG-1	ORG-2	OBG-3	Avg. final pob	Std. dev							
в	88000	88000	87000	89000	88000	1000	1.93E-04	0.25	0.29	0 7387	0 7162	1 97	

Page 2

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K	28000	5800	8600	6800	7067	1419	1.81E-04				assume B = B i	n inorg. test	4.92E-08
Cs	1400	70	30	60	53	21	4.01E-07			· · · · · · · · · · · · · · · · · · ·			1.13E-10
Inorg	anic anion varia	bility test											
	INORG-BLK	INORG-1	INORG-2	INORG-3	Avg. final ppb	Std. dev.							
В	<100	1800	2200	2300	2100	265	1.93E-04	0.25	0.25	0.7445	0.7243	1.83	
ĸ	29000	7800	7200	8000	7667	416	1.96E-04						5.02E-08
Ca	1300	70	70	60	67	6	5.02E-07				· · · · · · · · · · · · · · · · · · ·		1.32E-10
Wash	ing/Dilution Tes	<u>t</u>											
<u> </u>	3-78558	3-78559	3-78560	3-78561									
	W/D-5-BLK	W/D-5-1	W/D-5-2	W/D-5-3	Avg. tinal ppb	Sta. dev.	1.005.05					0.71	
ЦК ЦК	<100	200	180	190	190	10	1.002-00					0.71	1 205 08
K_	180000	58000	61000	61000	60000	1/32	2 415 06						2.995-11
	6700	400	4/0	490	453	4/	3.412-00						2.002-11
EXCES		<b>FT 4 4</b>	ET 4 0	ET 4 0	Aug fingt and	Ctal aloue							
<u> </u>	EI-I-DLA	E1-1-1	E1-1-2	EI-1-3			1 225 04	A 7	5 55	0 6906	0.4410	217.76	
B	520	100000	830	4400	1953	50007	1.005.02	<b>4.</b> /	5.55	0.0090	0.4418	217.70	2 425-05
<u> </u>	530000	120000	90000	0200	74007	159907	1.092-03						8 24E-08
	30000	660	440	<20	550	100	4.142-00						0.242-00
EXCes	S IFD LUSL	ET 0 1	ET 0 0	ET 22	Ava final pob	Std dov							
<u> </u>	E1-2-DLN	E1-2-1 6000	740	6000	Avg. IIIai pp0	2027	3.475-04	A 7	5 55	<u> 2083 0</u>	0 4410	217 76	
₽ ►	470000	3500	52000	6700	21067	27701	5 30E-04	4.7		0.0000	0.4410		1 80E-05
	470000	-20	33000	120	21007	#DIV/01	1.595-06						8 22F-08
Even	TPP tost	<20	210	<20	210	#019/01	1.562-00						0.222 00
	ET 2 PLK	ET 2 1	ET 2 2	ET-2-2	Ave final pob	Std. dov							
<b>—</b>	21-0-DLK 400	7600	6700	6700	7000	520	6 02E-04	47	5 55	0 6896	0 4410	217 76	
<b>P</b>	50000	5500	21000	7200	11233	8501	2 87F-04	4.1	0.00	0.0000	0.1110		1.66E-05
	20000	~20	21000	<20	#DIV/01	#DIV/01	#DIV/01						#DIV/0!
Staid	iometric sulfate	ion test (0.12	5 M)		*010/01	#01170.	*211/0.						
	S-Sulf-lon-Blk	S-Sulf-lon-1	S-Sulf-lon-2	S-Sulf-lon-3	Ava final opb	Std dev.							
B	100	1400	1500	1800	1567	208	1.36E-04	0.25	0.38	0.7258	0.6983	2.24	
K	29500	9100	7600	7500	8067	896	2.06E-04						4.39E-08
Ca .	1700	110	110	100	107	6	8.03E-07						1.77E-10
High	Temperature Sc	lubility Kinetics	(65 C)										
	HTK-1	HTK-2	HTK-3	нтк-4									
в	690	1800	1800	4200	2600	1386	1.77E-04	4.7	5.55	0.6896	0.4419	217.76	
ĸ	85500	5700	6300	6750	6250	527	1.60E-04						2.72E-06
Cs.	825	<30	<30	<30	#DIV/0!	#DIV/0!	#DIV/0!						#DIV/01
High	Temperature Sc	lubility (65 C)											
	HTS-5-BLK	HTS-5-1	HTS-5-2	HTS-5-3						· · · · · ·			
в	325	6150	6750	6750	6550	346	5.76E-04	0.047	0.05	0.7750	0.7662	0.98	
ĸ	212500	16500	16500	14700	15900	1039	4.07E-04						1.75E-07
Cs	11875	30	105	45	60	40	4.51E-07						1.96E-10
High	Temperature So	olubility (65 C)											
	HTS-4-BLK	HTS-4-1	HTS-4-2	HTS-4-3									
в	325	5550	6150	6000	5900	312	5.16E-04	0.141	0.15	0.7595	0.7449	1.44	
K	225000	21000	22500	21000	21500	866	5.50E-04						3.04E-07
Cs	12500	195	195	195	195	0	1.47E-06						8.27E-10

#### High Temperature Solubility (65 C) HTS-3-3 HTS-3-BLK HTS-3-1 HTS-3-2 0.6751 2.56 0.47 0.5 0.7094 6300 6450 5400 6050 568 5.18E-04 450 24000 22000 1732 5.63E-04 21000 262500 21000 240 225 240 15 1.81E-06 16250 255 High Temperature Solubility (65 C) HTS-2-BLK HTS-2-1 HTS-2-2 HTS-2-3 0.5977 0.5086 5.37 3.75E-04 1.41 1.54 250 4500 3900 4500 4300 346 15000 11850 14850 13900 1777 3.56E-04 300000 195 135 165 30 1.24E-06 17500 165 High Temperature Solubility (65 C) HTS-1-BLK HTS-1-1 HTS-1-2 HTS-1-3 0.6896 0.4419 217.76 1245 2065 1089 1.36E-04 4.7 5.55 600 1650 3300 5250 4800 6000 5350 606 1.37E-04 412500 2 2.26E-08 25000 5 2 2 3 Intermediate Temperature Solubility (50 C) ITS-1-BLK ITS-1-1 ITS-1-2 ITS-1-3 2.56 0.47 0.5 0.7094 0.6751 2375 3750 3900 4500 4050 397 1.55E-04 11000 1258 2.81E-04 287500 12450 10350 10200 105 75 90 15 6.77E-07 16250 90 Sodium sulfate (0.125 M), no potassium SulfOK-BLK SulfOK-1 Sulf0K-2 Sulf0K-3

2.44E-05

8.27E-06

8.93E-05

0.25

в

κ

Cs

в

κ

Cs

в

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Cs

В

ĸ

C6

в

ĸ

Cs

<100

180

160000

420

580

7900

600

130

16700

310

260

11000

443

323

11867

146

232

4464

#### Sheet1

ι.

5.03E-07

1.70E-09

3.63E-07

1.49E-09

1.78E-06

4.59E-10

7.52E-08

1.90E-10

3.16E-10

3.54E-09

2.24

0.7258

0.38

0.6983

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<b>Kinetics</b> Tests								· · ·		
	HIK-BLK-1	HIK-BLK-2	[Na] = 4.7 M							
В	663	676								
K	728000	819000								
Cs	39000	46800								
									×	
	HIK-1	HIK-2	HIK-3	HIK-4	HIK-5	HIK-6	HIK-7	HIK-8	HIK-9	HIK-10
B	559	546	585	598	559	572	559	572	559	585
ĸ	234000	234000	182000	234000	130000	143000	156000	156000	124800	122200
Cs	1690	1950	1170	1430	689	702	806	767	520	637
hours	48	48	72	72	144	144	192	192	240	240
K (KTPB)										
K (CsTPB)										
		-								
Stoichiometric	TPB, moderate	ionic strength	kinetics test							
	SMK-1 (bik)	SMK-2 (blk)	[Na] = 1.41 M							
B	• 78	39								······
K	113100	88400								
Cs	7280	6370					· · ·			
,	SMK-3	SMK-4	SMK-5	SMK-6	SMK-7	SMK-8	SMK-9	SMK-10		
B	1820	1300	1690	2600	1820	1690	1001	988		
K	5720	6890	7670	4030	3900	4550	15600	7540	-	
Cs	<26	<26	<26	<26	<26	<26	52	<26		
hours	4	4			23.5	23.5	32	32		
Excess TPB Hi	gh ionic strengt	h Kinetics test	(no blanks)			<b>E</b> 1116 0				
	EHK-1	EHK-2	EHK-3	EHK-4	EHK-5	EHK-6	EHK-/	EHK-8	ENK-9	ENA-10
В	663	572	546	520	520	520	520	533	520	507
ĸ	299000	312000	260000	286000	221000	195000	169000	182000	9880	102700
Cs	2860	2340	1690	1950	1274	975	780	884	3//	364
hours	24	24	48	48	72	72	96	96	192	192

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			and the second se								
Sodium	Tetraphenylborate so	lubility									
		dil'n corrected		dil'n corrected		dil'n corrected		dil'n corrected			
	SNA-1-BLK	SNA1-BLK	SNA-1-1	SNA1-1	SNA-1-2	SNA1-2	SNA-1-3	SNA1-3	Average	[B or Na] (M)	init. [Na] (M)
В	<0.5	#VALUE!	<0.5	#VALUE!	<0.5	#VALUE!	<0.5	#VALUE!	#VALUE!	#VALUE!	
Na	95250	100012.5	93960	. 103356	91140	100254	89870	98857	100822.	4.386	4.700
	SNA-2-BLK	SNA2-BLK	SNA-2-1	SNA2-1	SNA-2-2	SNA2-2	SNA-2-3	SNA2-3		N	
В	<0.5	#VALUE!	351	386.1	440	484	488	536.8	469.	0.043	
Na	51280	53844	44810	49291	42980	47278	44180	48598	48389.	2.105	2.350
	SNA-3-BLK	SNA3-BLK	SNA-3-1	SNA3-1	SNA-3-2	SNA3-2	SNA-3-3	SNA3-3			
В	1672	1755.6	1738	1911.8	756	831.6	791	870.1	1205.	0.111	
Na	20280	21294	21810	23991	22380	24618	23270	25597	24735.	1.076	0.940
	SNA-4-BLK	SNA4-BLK	SNA-4-1	SNA4-1	SNA-4-2	SNA4-2	SNA-4-3	SNA4-3			
В	108	113.4	1.617	1778.7	1775	1952.5	1711	1882.1	1871.	0,163	
Na	10970	11518.5	17930	19723	18080	19888	18100	19910	19840.	0.863	0.470
	SNA-5-BLK	SNA5-BLK	SNA-5-1	SNA5-1	SNA-5-2	SNA5-2	SNA-5-3	SNA5-3			
В	210	220.5	3262	3588.2	3477	3824.7	3628	3990.8	3801.	0.332	
Na	2893	3037.65	18490	20339	17160	18876	17700	19470	19562.	0.851	0.141
						· · · · · ·					
	SNA-6-BLK	SNA6-BLK	SNA-6-1	SNA6-1	SNA-6-2	SNA-6-2	SNA-6-3	SNA6-3			
В	0.1	0.11	15	16.5	16.8	18.48	16.9	18.59	18.	0.0016	
Na		0		0		0		0	0.	4.230	4.230
Sodium t	etraphenylborate sol	ubility at 65 C	,								
	SNA-7-BLK	SNA7-BLK	SNA-7-1	SNA7-1	SNA-7-2	SNA-7-2	SNA-7-3	SNA7-3		•	
В	0	0	244.6	366.9	295.1	442.65	285.1	427.65	412.	0.0381	
Na		0		0		0		0	0.		2.350

				······						
						ļ				
										Assume K3=0
calc'd Na (M)	density (g/mL	wt. diss. solid	Na molality	[monoanion]m	[div.anion] m	Ionic Str. I	Na act. coeff.	TPB act.coeff.	К3	TPB act. coeff.
	1.210	321.70	4.935	4.315	0.310	5.25	0.575	180.19	#VALUE!	#VALUE!
4.700										
										5
	1.091	160.85	2.262	1.947	0.158	2.42	0,583	14.46	0.87500962	10.25
2.393	1									
	· · · · · · · · · · · · · · · · · · ·									
	1.060	110.86	1.134	0.995	0.069	1.20	0.629	4.06	0.29937626	8.41
1.051										
									•	
	1.056	166.67	0.971	0.887	0.042	1.01	0.639	3.59	0.23678322	9.40
0.633					·		· · · · · · · · · · · · · · · · · · ·			
						·				
· · · · · · · · · · · · · · · · · · ·				·				-		
	1.036	252.59	1.086	1.024	0.031	1.12	0.634	3.83	0.38158316	6.22
0.473		1								
			<u> </u>							
•	1.179	289.53	4.755	4.196	0.279	5.03	0.571	156.87	0.62268052	156.19
4.232										
			,							
	1.104	173.90	2.568	2.253	0.158	2.73	0.575	20.58	1.07886777	11.83
2 388							1	ELEVATED TEM	PERATURE EXP	