DECONTAMINATION OF HIGH-LEVEL WASTE USING A CONTINUOUS PRECIPITATION PROCESS

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ABSTRACT

This study provided a first of a kind demonstration of the decontamination of High Level Radioactive Waste from the Savannah River Site using a continuous precipitation/adsorption process. Testing used a composite sample obtained from a number of waste tanks at the Savannah River Site. Preliminary batch processing experiments determined the efficacy of continuous process to precipitate sodium, potassium and cesium tetraphenylborate. The tetraphenylborate effectively removes cesium from solution. Researchers were also able to use the results of the batch experiments in design and prediction of the operation of the continuous process. This demonstration used two continuous reactors in series. This paper details the results obtained from batch tests with simulant and continuous decontamination of actual High Level Waste from the Savannah River Site.

INTRODUCTION

In the early 1980's, the Savannah River Site developed a process for isolating radioactive cesium from a highly alkaline solution.[1] This process involved the

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precipitation of the cesium ions with tetraphenylborate to achieve the required 7,000 to 40,000 decontamination factor that is required for disposal of the bulk salt solution. The process concentrated and washed the resultant precipitant to remove the high concentration of sodium ions from the bulk precipitate. The Savannah River Site developed a flowsheet for the application of this technology based on the use of existing 1.3 million-gallon high level waste tanks as the reaction vessels. However, during startup of this facility, the ability to safely operate this process in such large reaction vessels became questionable.[2] Subsequently, personnel developed an alternative flowsheet employing this same precipitation process.[3] This proposed process relies upon smaller tanks to mitigate the safety hazards associated with the initial application of this chemistry. The primary advantages of the smaller tanks are associated with increased assurance of maintaining an inert atmosphere in the tanks and in reducing contact time in the tanks. The proposed process involves the continuous precipitation of cesium in a series of stirred tank reactors. The use of a continuous process in place of the previous batch process requires further understanding of the underlying precipitation chemistry. The primary objective of this work was to provide a first of a kind demonstration of the proposed continuous precipitation process with a sample of High Level Waste (HLW) obtained from the Savannah River Site (SRS) HLW tank farm. In addition, this work was intended to increase the basic understanding of precipitation processes.

EXPERIMENTAL METHODS

This work occurred in two segments. The first segment involved batch precipitation studies using simulated waste solutions. The second segment involved a continuous precipitation test using waste from the SRS HLW tank farm. Table 1 provides the composition of a typical simulated salt solution. The salts were dissolved with deionized water in a flask. The final sodium ion molarity of the solution was confirmed by density measurement. Initial solution preparation omitted

Table 1. Composition of 5.85 M [Na+] Simulated Salt Solution

Component	Concentration (M)
NaOH	3.00
$AL(NO_3)_3*9H_{20}$	0.35
$NaNO_3$	1.47
$NaNO_2$	0.85
Na_2CO_3	0.20
$Na_2SO_4*10H_{20}$	0.07

sodium tetraphenylborate (NaTPB), cesium nitrate (CsNO$_3$), and potassium nitrate (KNO$_3$). In a separate stock solution, NaTPB was prepared by adding NaTPB solids to a 0.1M sodium hydroxide (NaOH) solution to provide a NaTPB concentration of 0.5 M. Separate stock solutions of CsNO$_3$ (0.24 M) and KNO$_3$ (1.5 M) were also prepared. All stock solutions used deionized water with the concentrations of each stock confirmed through various analyses. Cesium and potassium determinations used atomic adsorption (AA) while the measurement of NaTPB concentration employed High Performance Liquid Chromatography (HPLC). The use of separate solutions containing CsNO$_3$, KNO$_3$ and NaTPB provided the ability to adjust the ratio of these species in solution independently. Note, however, that in all cases the cesium concentration was more than an order of magnitude less than the potassium concentration.

All the batch precipitation reactions occurred in stainless steel reaction vessels with baffles, and were placed in a water bath to maintain a temperature of 25$\pm$3 °C. Two types of batch precipitation reactions occurred. The first type of batch experiments were intended to determine if sodium tetraphenylborate co-precipitated with potassium and cesium tetraphenylborate. For the first type of batch reactions, two 250-mL glass flasks of the various stock solutions were prepared. One flask contained the simulated salt solution, CsNO$_3$, KNO$_3$, and dilution water as required to fill to 250 mL. The other flask contained simulated salt solution, NaTPB (at less than the solubility limit for the solution sodium concentration), and dilution water. In both flasks, the volume of dilution water was adjusted to obtain bulk solutions with equal sodium concentration. The solutions in the two flasks were combined by pouring simultaneously into the stainless steel reaction vessel and agitating for ten minutes with an overhead stirrer at ~300 rpm.

After ten minutes, the contents were filtered (with a 0.45-micron disposable filter) and the resulting filter cake was washed with two 5-mL portions of deionized water. Analyses of the supernate and the wash water included (AA) for sodium (Na) and potassium (K), HPLC for tetraphenylborate (TPB), and inductively coupled plasma-mass spectrometry (ICP-MS) for cesium (Cs). Selected solid samples were submitted for x-ray diffraction (XRD) analysis and for chemical analysis.

The second type of batch experiments were intended to simultaneously investigate the dissolution rates of insoluble sodium tetraphenylborate and determine the soluble tetraphenylborate concentration at equilibrium for crystals of a mixture of sodium and potassium tetraphenylborate. The experimental protocol for the second type of batch experiments differed in two ways from the previous tests: the method for adding the stock solutions to the reaction vessel and the experiment duration. From previously prepared stock, CsNO$_3$, KNO$_3$, simulated salt solution and deionized water were added to the reaction vessel and agitation begun. Then, the desired amount of NaTPB solution was added drop-wise using a burette. Note that the quantity of NaTPB added for some of these tests did exceed
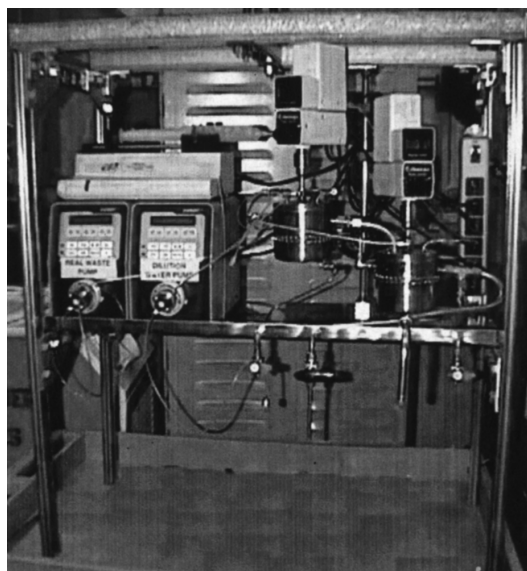
Figure 1. Equipment for continuous precipitation.

the soluble amount. All experiments with sodium ion concentration ranging from 0.2 M to 4.5 M were agitated for 24 hours. After 24 hours, the samples were filtered. Experiments with the sodium ion concentration of 5.0 M lasted for 72 hours. Periodically (after 1, 3, 9, 24, 48, 72 hours) throughout the test, samples were obtained and filtered.

Figure 1 contains a picture of the experimental equipment employed during the continuous process demonstration. Personnel conducted the experiment remotely within the SRS Shielded cells. The test used two pumps (to the left of the picture) to deliver the waste (at 0.73 mL/min) and the NaTPB solution (at 0.27 mL/min) to the first of two reaction vessels (center right of the picture). Each of the reaction vessels had a 500 mL working volume and contained 2 inch pitched blade Litghtin A200 impellers operated at 400 rpm. In addition, each of the reaction vessels contained 4 side wall baffles (each $1/12^{th}$ the diameter of the vessel) and a draft tube around the impeller and shaft (extended from roughly ¼ of the vessel working height to ¾ of the vessel working height). The desired flow rates for the waste and NaTPB solution pumps were adjusted prior to transfer of the equipment to the Shielded Cells. The continuous stirred tank reactors (CSTRs) were initially filled by pumping the 6.4-M [Na] salt solution (obtained from Tank 44F at SRS) and deionized water resulting in a [Na] concentration of 4.7 M. Effluent from the first CSTR completely filled the second CSTR, by means of overflow. During the filling process, the feed rates of the two streams were measured and final adjustments

were made to achieve the desired feed flow rates. After completely filling both CSTRs, the experiment was initiated by pumping the salt solution and a mixture of 0.31 M NaTPB dilution water and monosodium titanate (MST) into the first CSTR. Sufficient MST was added to bring the steady state concentration of MST to 0.4 g/L. The MST is added to remove strontium and actinides from solution. It is not anticipated that this adsorbent will have any impact of the precipitation reactions. This experiment employed a TPB to potassium ratio of 1.6. The material from Tank 44F was analyzed and determined to contain 62-mM potassium.

The available tank waste material for this test allowed a duration of 80 hours. However, the formation of foam in the reaction vessels led to frequent interruptions of overflow from the second reactor, and eventually interrupted the overflow from the first reactor. Figure 2 provides an indication of the nature of foam formed by this process. (Note, the picture in Fig. 2 was obtained from a previous test that was also terminated due to foaming problems.) Also, the feed of NaTPB solution stopped on two occasions due to fouling of the pump head by MST particles. The second of these two interruptions coincided with the interruption of overflow from the first reactor. These experimental difficulties prevented restoration of stable operations of the unit and steady state performance could not be re-established after 50 hours of operation.

Figures 3 and 4 contain the x-ray diffraction (XRD) patterns for pure NaTPB and KTPB, showing little difference between the two crystal structures.
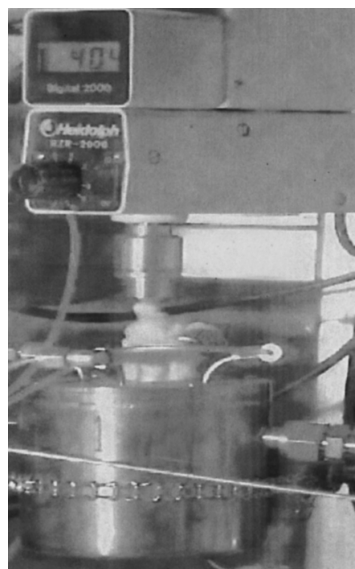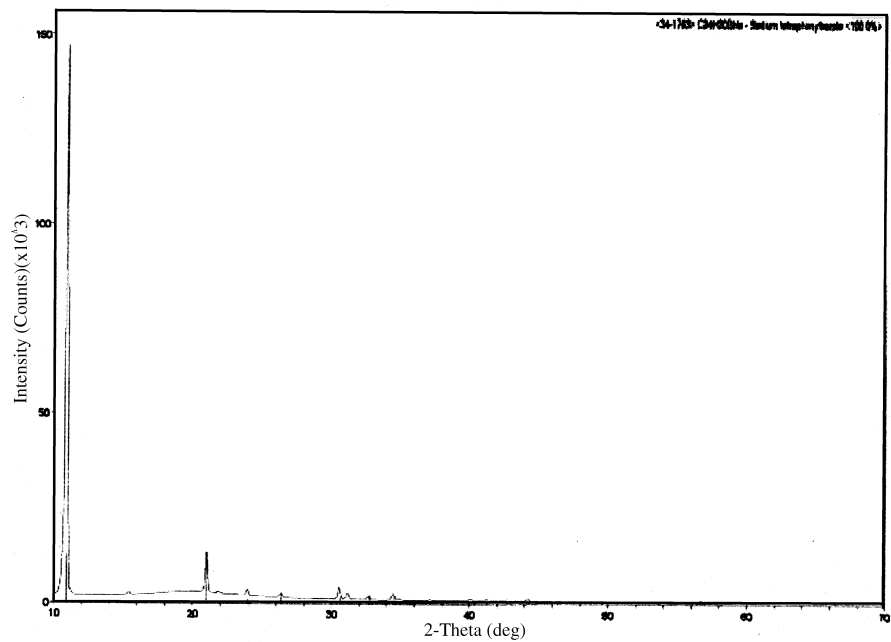

Figure 2. Form from reactor vessels.

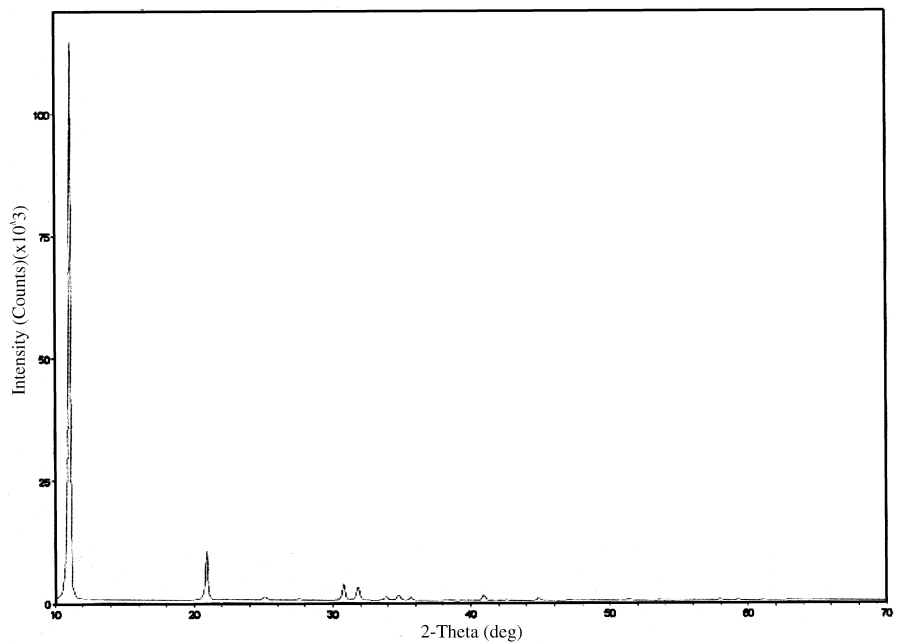***Figure 3.*** X-ray diffraction pattern for pure NaTPB.

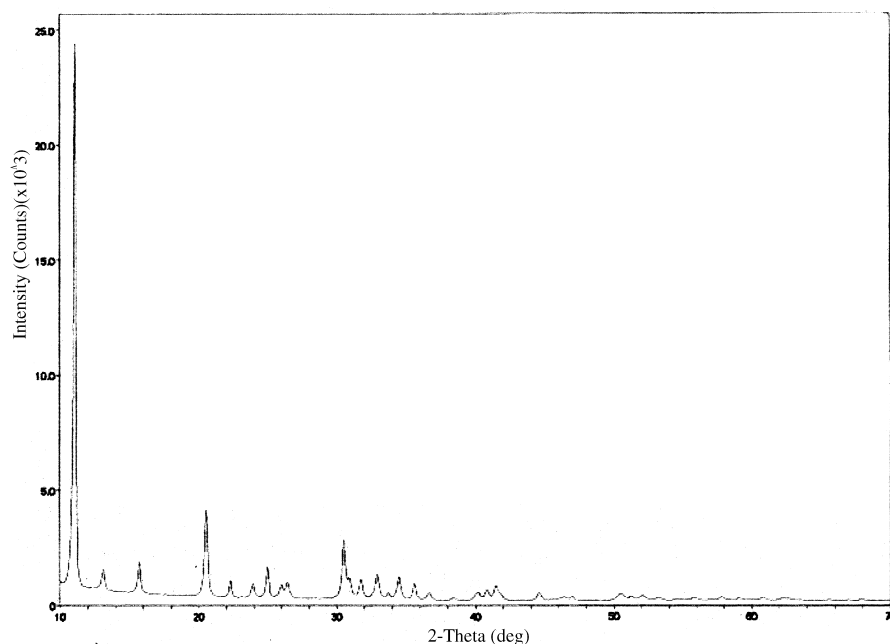***Figure 4.*** X-ray diffraction pattern for pure KTPB.

Figure 5. X-ray diffraction pattern pure CsTPB.

Given the similarity of the NaTPB and KTPB XRD patterns, other means are required for analyzing the solid sample that could contain both NaTPB and KTPB. Figure 5 contains the x-ray diffraction pattern for pure CsTPB, which differs from that of NaTPB and KTPB at 13 and 16 theta. At 13 and 16 theta, two small peaks exist in the x-ray diffraction pattern CsTPB and none for NaTPB and KTPB. Note that these reflections may occur in the NaTPB and KTPB, but do not have sufficient intensity to be easily observed. Therefore, the presence of these two peaks allows one to easily distinguish CsTPB from NaTPB and KTPB. Figure 6 contains the x-ray diffraction pattern for a sample of co-precipitated material. Inspection of this figure indicates the presence of the two peaks at 13 and 16 theta. The pattern for this mixed crystal combined with chemical analyses of the solids suggests that the resultant crystal is a mixture of all three species in a single crystalline phase.

RESULTS AND DISCUSSION

To help determine the required residence time in the CSTRs, it is useful to perform a material balance on tetraphenylborate ion in solution and insol-
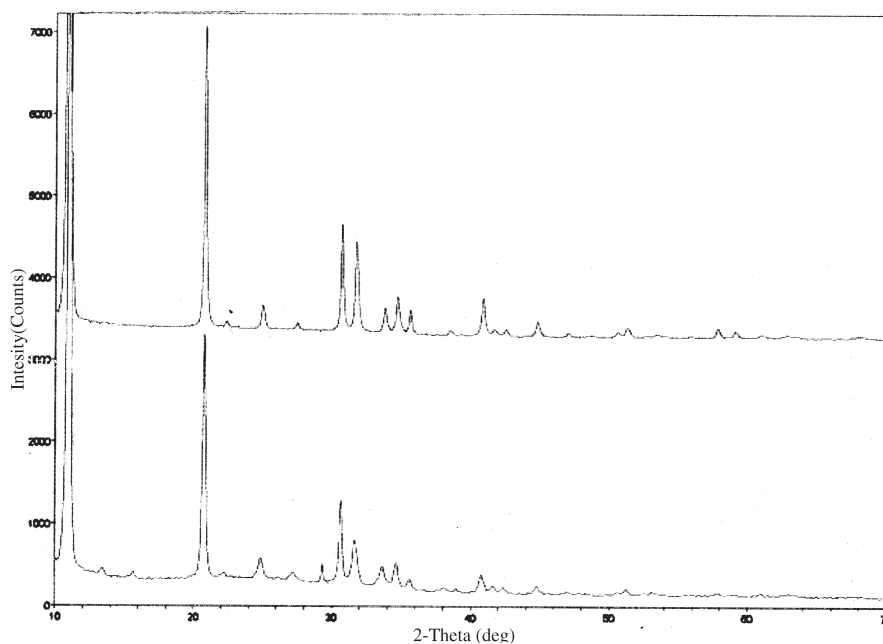
Figure 6. X-ray diffraction pattern for mixed precipitated.

uble sodium tetraphenylborate. Sodium tetraphenylborate entered all of these reaction processes as a soluble species. The desired reactions of interest follow.

$$K^+ + TPB^- \xleftrightarrow{K_{sp}} KTPB$$
$$Cs^+ + TPB^- \xleftrightarrow{K_{sp}} CsTPB$$

Eqn. 1,2

However, a competing reaction also occurs when mixing NaTPB solution with high sodium molarity waste streams:

$$N_a^+ + TPB^- \xleftrightarrow{K_{sp}} N_aTPB$$

Eqn. 3
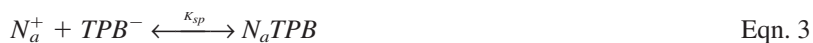
Consider the case of a single drop of solution containing tetraphenylborate entering the stirred tank reactor. This droplet has a specified volume (V), sodium molarity (N) and tetraphenylborate molarity (M). This droplet will encounter a second volume (X) of salt solution that has a fixed sodium molarity (N'). For the sake of illustration, we will assume the second volume of salt solution does not contain any soluble tetraphenylborate. The sodium molarity of this drop equals

that of the bulk CSTR. Mixing the two volumes together yields a new equilibrium as given by the following equations.

$$V_i = V + X$$
$$N_i = \frac{V * N + X * N'}{V_i} \qquad\qquad \text{Eqn. 4,5,6}$$
$$M_i = \frac{V * M}{V_i}$$

Fixing V as 1 mL, one can solve for X as a function of N_i.

$$X = \frac{N_i - N}{N' - N_i} \qquad\qquad \text{Eqn. 7}$$

Substituting for X yields M_i as a function of N_i.

$$M_i = \frac{M}{1 + \left(\dfrac{N_i - N}{N' - N_i}\right)} \qquad\qquad \text{Eqn. 8}$$

This formula provides the total tetraphenylborate molarity (both soluble and insoluble) in mixed droplet, M_i, as a function of the sodium molarity of the mixed droplet. Figure 7 contains a plot of the curve defined by this equation for the following variable values.

M = 0.3 M

N = 0.3 M

N' = 4.7 M

The solubility of tetraphenylborate in the absence of potassium and cesium was measured employing the second type of batch experiments described above. Figure 7 also contains a plot of the experimentally measured solubility data and a fit to the data. The fit is of the form:

$$M_{i,s} = e^{(0.58 - 1.45 N_i)}$$

Inspection of Fig. 7 indicates that, as the solution mixes, the solution will exceed the sodium tetraphenylborate solubility. Thus, under many conditions of interest, precipitation of NaTPB will likely occur. For the example shown in Fig. 7 (those of the CSTR test performed in the shielded cells), 88% of the TPB⁻ added to the reactor can precipitate as NaTPB. The maximum extent of precipitation occurs when the sodium molarity (N_i) in the mixing volume is 4.0. At this condition, the solubility of NaTPB is 0.0057 M while the concentration in the mixing zone is 0.0478. Under these conditions, 88% of the tetraphenylborate added would precipitate.
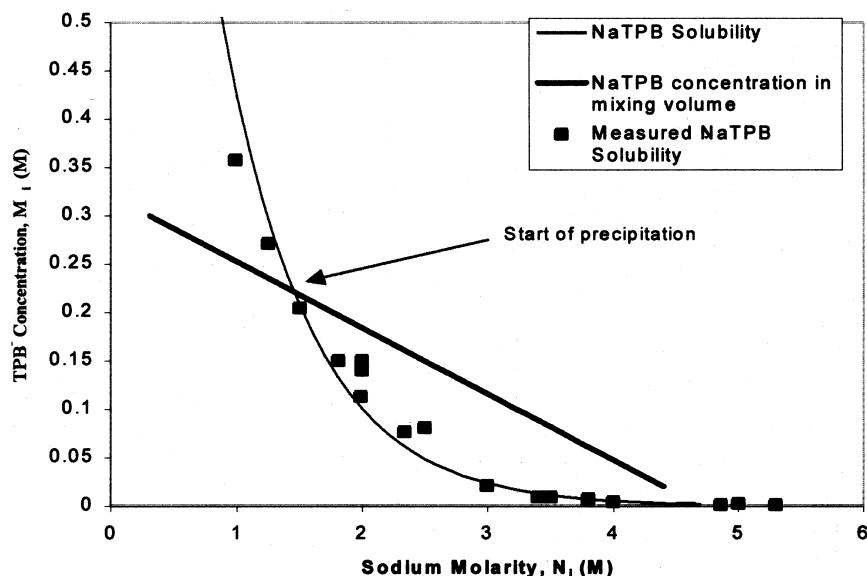
Figure 7. Tetraphenylborate (TPB) concentration as a function of sodium molarity.

Batch Precipitation Test Results

Inspection of Fig. 8 verifies the occurrence of this precipitation phenomenon. Figure 8 contains a plot of the soluble potassium concentration following a batch precipitation reaction where NaTPB was added as 0.55 M solution (the second type of batch experiment described above). Figure 8 contains the data from two experiments, one with TPB added in equal stoichiometric ratio to the quantity of potassium plus cesium in solution and one test with 91% of the stoichiometric ratio. Both experiments shown contained 850 mg/L K^+ prior to the start of the precipitation reaction. Inspection of the figure indicates significant ($>$40%) precipitation of KTPB by the first sampling (i.e., at 30 minutes). This decrease is associated with the simultaneous precipitation of NaTPB, KTPB and CsTPB. Note that throughout the duration of this test, the concentration of soluble tetraphenylborate remained below the detection limit (by HPLC). These results indicate that during the initial mixing of the salt solution and the tetraphenylborate that the majority of the tetraphenylborate precipitated as NaTPB. Note, however, that as the solution continually mixed, NaTPB dissolved allowing the subsequent precipitation of KTPB and CsTPB. Also note that, as one would expect, this reaction appears first order in NaTPB solids (see below). Note that since cesium is present at significantly lower concentration than potassium, the impact of the cesium can be neglected.
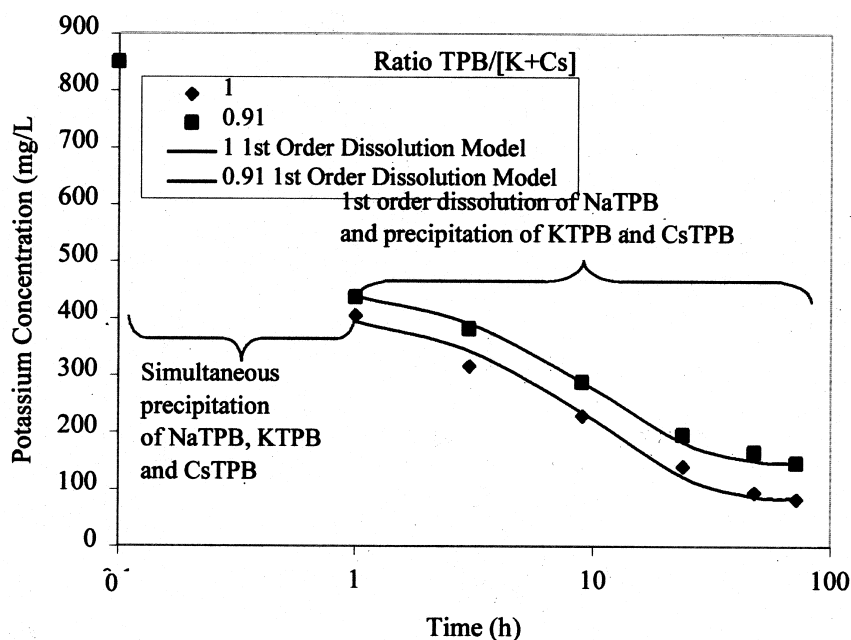
Figure 8. Potassium concentration during batch precipitation reaction.

Further inspection of Fig. 8 indicates that this dissolution reaction reached its endpoint by approximately 72 hours. Also note that for the TPB⁻/K ratio of 1, approximately 80 mg/L of potassium remain in solution after 72 hours. This result indicates that even at apparent equilibrium, a significant portion of the NaTPB (10%) remains in an insoluble form. Figure 8 also contains a fit to the potassium data assuming first order dissolution kinetics for the available NaTPB (i.e., the NaTPB in excess of the 10% that does not dissolve). The fit results in the following expression for the dissolution of NaTPB (with time in hours).

$$\frac{d[NaTPB]}{dt} = -0.09 hr^{-1}[NaTPB] \qquad \text{Eqn. 9}$$

One can obtain additional insight into the nature of the NaTPB by examining the steady state soluble TPB⁻ concentration for a variety of TPB⁻/K ratios. Figure 9 contains a plot of such data. Inspection of this figure indicates that the TPB⁻ concentration increases as a function of the TPB⁻/K⁺ ratio. Figure 9 also contains an estimate of this solubility. Inspection of Fig. 9 indicates that the concentration of TPB⁻ in solution appears to approach the concentration present for pure NaTPB as the TPB⁻/K⁺ ratio increases. A simple exponential decay could therefore be used. Also, the solubility decreases to that of KTPB as the ratio of TPB⁻/K⁺ ap-
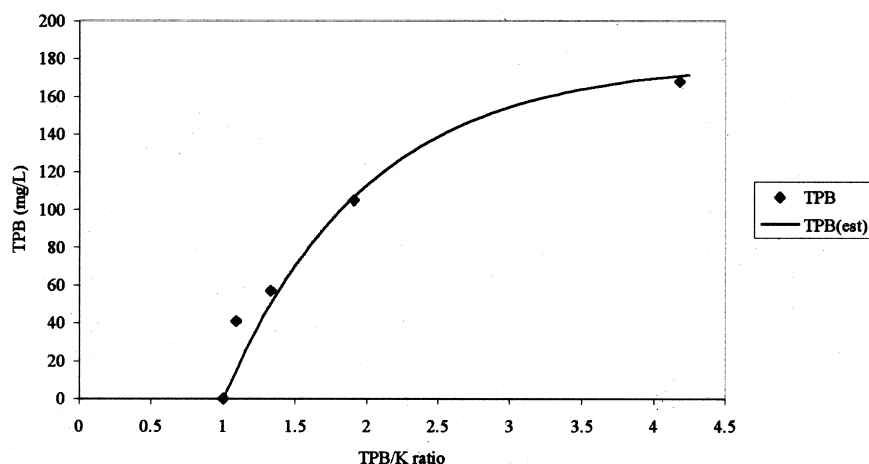
Figure 9. Tetraphenylborate (TPB) concentration versus TPB/K ratio for the 72 hour experiment.

proaches 1; an exponential of (1- TPB$^-$/K$^+$) will provide this functionality. Finally, an estimate using the following simple exponential expression is developed:

$$M_s = \left(1 - \exp\left(1 - \frac{TPB^-}{K^+}\right)\right)M_{NaTTB} + M_{KTPB} \qquad \text{Eqn. 10}$$

where M_{NaTPB} represents the solubility of pure NaTPB, in this case taken as 178 mg/L (found by minimizing the error from the fit to the data). These results suggest that the crystalline phase contains neither a mixture of only CsTPB and KTPB nor pure NaTPB but rather a mix of all three crystalline phases. As the ratio of NaTPB in the crystal phase increases, the solubility approaches that of the pure NaTPB.

Further evidence for the formation of these mixed crystalline phases comes from the first set of batch experiments performed. The design of these experiments avoided exceeding the local solubility of NaTPB, and as such precluded the precipitation of NaTPB as outlined. Subsequent to the formation of solids, the slurry was filtered and the resultant precipitate was washed. Analysis of the wash water indicated the presence of TPB$^-$, but no K$^+$ or Cs$^+$. Figure 10 contains a plot of the amount of TPB$^-$ in the wash water as a function of the sodium molarity. Note that the variability in the data of Fig. 10 for various sodium molarities likely results from a number of other experimental factors including the differing TPB$^-$/K$^+$ ratios in the tests. However, a trend in the quantity of TPB$^-$ in the wash water as a function of the ratio appears inconsistent. The presence of TPB$^-$ in the wash water indicates that some NaTPB co-precipitated with the KTPB and CsTPB.
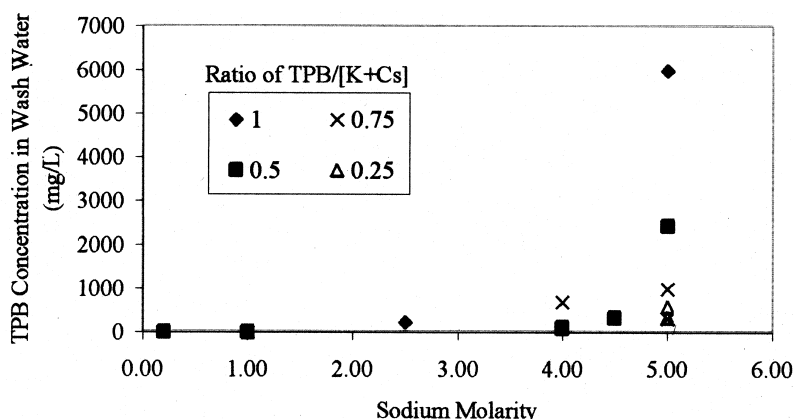
Figure 10. Tetraphenylborate (TPB) in the wash water (with TPB^-/K^+ as variable).

CSTR Test Performance Results

Taken as a whole, results from the batch tests can be used to predict the performance of the CSTR. As indicated above, 12% of the TPB^- added to the reactor will remain in solution following mixing of the chemicals in the experiment using Tank 44F waste. This results in a net addition rate of 0.01 mmole/min of soluble TPB^-. The minimum quantity of NaTPB that can exist in the system and remain available for dissolution is the 60% excess material added in the feed stream. This excess equates to 26 mM in the feed stream, which for the total working volume of both reactors equates to 26 mmoles. Since the rate constant for dissolution is 0.0015 min^{-1} (see Eqn. 9), the dissolution rate becomes 0.039 mmole/min. Potassium was added to the system at a rate of 0.045 mmole/min (note that cesium was added to the system at a rate of approximately 0.1 μmole/min). Based on these calculations, the rate of addition of TPB^- to the total reaction system should prove sufficient to achieve decontamination of the waste solution. Figure 11 contains a plot of the soluble cesium concentration leaving the second reactor as a function of time. Inspection of this figure indicates that the cesium in this stream had, as expected, been removed from solution. Note that a loss of tetraphenylborate feed occurred after about 40 hours and lasted for a short duration (~2 hours). However, decontamination of the salt solution quickly recovered once the tetraphenylborate flow was re-established. A number of other experimental difficulties occurred during the continuous operation of this test. The most significant of these difficulties involved the formation of foam in the reaction vessels. Figure 2 provides an example of the type of foam formed in these reaction vessels. Note, however, that since the first indications of foam formation occurred after approximately 20 hours of operation,
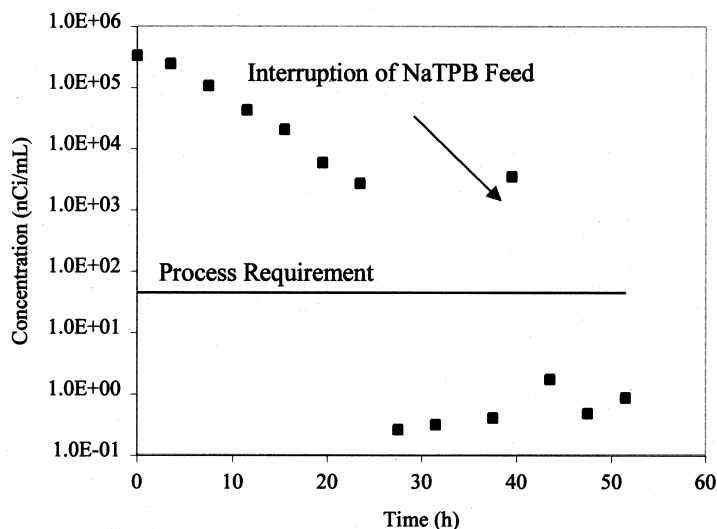
Figure 11.   Cesium concentration as a function of time from CSTR test.

this foam formation does not appear to interfere with the ability to decontaminate the salt solution using this precipitation reaction. However, the presence of foam may significantly impact the hydraulic performance of the proposed facility. Future work will asses the utility of antifoam agents in preventing the formation of foam in the reaction vessels.

CONCLUSIONS

Batch tests shed insight into the precipitation of cesium and potassium tetraphenylborate. These tests indicate that upon the addition of soluble tetraphenylborate ion to high sodium bearing wastes, a significant quantity of sodium tetraphenylborate precipitates. This sodium tetraphenylborate precipitation occurs due to both exceeding the local solubility limit of sodium tetraphenylborate and due to co-precipitation of sodium tetraphenylborate with cesium and potassium tetraphenylborate. Based on the batch precipitation data, the authors developed an estimate of continuous reactor performance. These results were confirmed through performance of a test with High Level Waste from the Savannah River Site. This continuous test achieved the required level of cesium decontamination for the proposed treatment process.

ACKNOWLEDGMENTS

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