

## SEPARATIONS

# Continuous-Flow Process for the Separation of Cesium from Complex Waste Mixtures

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A continuous-flow process is proposed for the separation of Cs from complex, strongly alkaline, aqueous mixtures. This process, which includes the use of tetraphenylborate (TPB) anions to precipitate cesium from the bulk waste, minimizes the exposure time of TPB to the alkaline mixture by injecting TPB as a countercurrent into a small stream of the bulk waste and immediately following with filtration. The recovered solids are dissolved in propylene carbonate, and cesium is then extracted into an aqueous solution, to be later recovered as CsNO<sub>3</sub>, in a three-phase liquid–liquid–liquid extraction. Minimizing the time of exposure of TPB to strong (2 M) sodium hydroxide avoids the decomposition of TPB and subsequent release of benzene into the atmosphere above the reaction vessel.

### Introduction

Processing of <sup>137</sup>Cs waste at the U.S. DOE's Savannah River site (SRS) has currently been halted because of concerns over safety risks inherent in the current process.<sup>1</sup> The process in question, termed in-tank processing (ITP), entailed dissolving the mixture of <sup>137</sup>Cs-containing inorganic salts in water in million-gallon tanks, precipitating <sup>137</sup>Cs with sodium tetraphenylborate (NaTPB), and then filtering out the solids and passing the filtrate to the low activity waste process stream.<sup>2</sup> However, filtration of such large volumes requires thousands of hours, and during this time the tetraphenylborate (TPB) anion decomposes to form benzene and tri-, bi-, and monophenylboron.<sup>3</sup> While TPB was apparently believed to be stable in the approximately 2 M NaOH waste mixture,<sup>4,5</sup> prior work shows that TPB decomposes in even less basic solutions.<sup>6</sup> In addition, TPB is also subject to decomposition by radiolysis. The microdroplets of immiscible benzene formed in this process tend to coalesce, rise to the surface, and burst, thereby releasing a volatile and flammable organic compound into the atmosphere of the tanks. The dangers involved in the possible formation of a flammable atmosphere above tanks containing radioactive waste are obvious.

It is clear that the easiest and simplest means of decreasing benzene generation would be to reduce the period of time during which the TPB is exposed to <sup>137</sup>Cs and the alkaline waste solution. The precipitation of CsTPB is rapid upon the introduction of NaTPB(aq) to aqueous Cs<sup>+</sup> ions, so there is no need for the lengthy exposure times used in ITP. A continuous-flow process, in which NaTPB is introduced into a much smaller stream of waste solution by countercurrent injection and the composite stream is then passed immediately through the filtration process, would allow a rapid separation

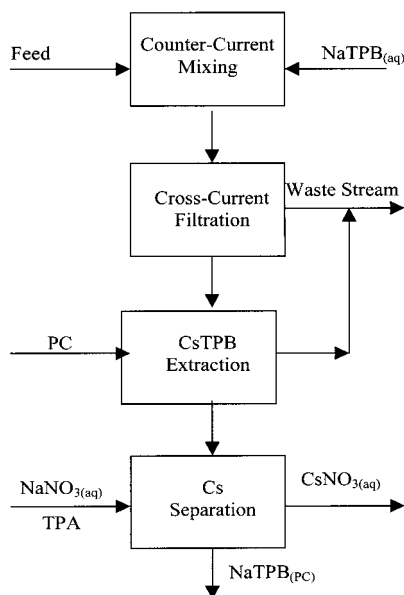
of Cs from the waste stream and minimize decomposition of TPB. Cross-current filtration yields a slurry of about 10% solids. While this solids content is significantly less than that which can be obtained by other methods of filtration, the reliability, simplicity, and reduction of exposure risks to plant personnel all speak strongly for the use of this type of filtration process.

A second problem with ITP is that it does not provide a directly processable product for final remediation of the filtered CsTPB. The slurry would require further processing before being passed to the Defense Waste Process Facility (DWPF) for vitrification.<sup>7</sup> Vitrification is currently the only method approved for final disposal of <sup>137</sup>Cs, provided that the glass is more durable than the previously assessed DWPF Environmental Assessment Glass.<sup>8</sup> Organic components in the slurry, such as TPB, can cause volume expansion and bubbling during the vitrification process, resulting in an unsuitable, cracked, and porous glass. Without a provision for further processing of the Cs waste, ITP cannot be said to perform any <sup>137</sup>Cs remediation because the Cs slurry, which contains a mixture of organic and inorganic salts, can continue to decompose and form volatile benzene in storage.

CsTPB can be separated into its ionic components because it is soluble in a variety of solvents, including acetone, dimethyl sulfoxide, and propylene carbonate (PC). We have previously proposed a continuous process for the separation of Cs from a complex aqueous waste that would both minimize exposure of the TPB to decomposition agents and isolate the Cs as an inorganic salt suitable for immediate vitrification.<sup>10</sup> While this proposed process might have solved the remediation and process problems from a chemistry standpoint, it had several problems that prevented its implementation beyond a laboratory scale.

One of these problems was the use of small amounts of HCl in the process. Chloride ions are corrosive to the steel used in the plant fixtures and pipes. However,

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**Figure 1.** Proposed continuous-flow process for remediation of  $^{137}\text{Cs}$  waste at SRS.

nitrate salts could be easily substituted for HCl, forming  $\text{CsNO}_3$  rather than  $\text{CsCl}$  as the final product. More importantly, the acetone solvent proposed in the process is a flammable and volatile liquid and a SARA-listed chemical. Substitution of a safer solvent for acetone is clearly desirable. In addition, the recycling of nearly all of the process components necessitated a complex process with many steps. The danger of exposure entailed in the handling of radioactive compounds strongly favors a simpler process that reduces the risks to workers and public health and safety. Also, the recycling of TPB in our original process is not necessarily an economic driver in a situation where contract purchase obligations have already been incurred for the expected lifetime of the plant.

In this paper, we propose a simplified continuous-flow process to remediate Cs from the mixture formed by solvating the stored wastes at SRS. We have attempted to hew as close as possible to existing plans, materials, and plant footprint. Decomposition of TPB is minimized by injecting TPB into a small waste stream as a countercurrent, followed by immediate filtration. The recovered solids are dissolved in PC, and cesium is then ion-exchanged into water in a three-phase, liquid-liquid-liquid extraction.<sup>11</sup> The Cs end product of this process may be directly added as an aqueous solution to the high activity waste stream, or it may be evaporated to a mixture of  $\text{CsNO}_3$  and other alkali nitrate salts. (See Figure 1.)

## Experimental Section

NaTPB, tripropylamine (TPA), PC,  $\text{NaNO}_3$ , and  $\text{CsNO}_3$  were used as obtained from Aldrich. CsTPB was obtained by filtering and drying the precipitated product from a mixture of aqueous solutions of NaTPB and  $\text{CsNO}_3$ . Flame atomic emission spectroscopy (FES) was performed on a Perkin-Elmer 530 atomic absorption spectrometer. X-ray powder diffraction (XRD) was performed using a Phillips X'Pert MPD diffractometer. NMR was performed on a Bruker 360. Conductivity measurements were obtained using a YSI model 31 conductivity bridge (Yellow Springs Instruments, Yellow Springs, OH).

**Table 1.** Composition of the SRS Simulant

ionic component	concentration (M)	ionic component	concentration (M)
$\text{Na}^+$	5.6	$\text{SO}_4^{2-}$	0.15
$\text{Cs}^+$	0.00014	$\text{Cl}^-$	0.025
$\text{K}^+$	0.015	$\text{F}^-$	0.032
$\text{OH}^-$	1.91	$\text{PO}_4^{3-}$	0.010
$\text{NO}_3^-$	2.14	$\text{C}_2\text{O}_4^{2-}$	0.008
$\text{NO}_2^-$	0.52	$\text{SiO}_3^{2-}$	0.004
$\text{AlO}_2^-$	0.31	$\text{MoO}_4^{2-}$	0.0002
$\text{CO}_3^{2-}$	0.16		

**Table 2.** Solubilities and Limiting Molar Conductivities of Components of the Three-Phase System

compound	solvent	solubility at 24 °C (M)	limiting molar conductivity, $\Lambda_m$ ( $\text{S cm}^2 \text{mol}^{-1}$ )
$\text{NaNO}_3$	$\text{H}_2\text{O}$	10.8	120.8
NaTPB	$\text{H}_2\text{O}$	0.67	62.5
NaTPB	PC	2.6	16.0
NaTPB	PC satd <sup>a</sup>	2.2	
$\text{CsNO}_3$	$\text{H}_2\text{O}$	1.0	151.2
CsTPB	$\text{H}_2\text{O}$	$7.4 \times 10^{-5}$	
CsTPB	PC	0.041	19.6
CsTPB	PC satd <sup>a</sup>	0.035	
KTPB	PC	0.19	
H-TPA-TPB	PC	0.98	

<sup>a</sup> PC saturated with water.

The fractions of initial cesium concentrations removed from test mixtures were determined by FES analysis of the Cs remaining in the PC phase of the system. The error in these determinations, determined from serial dilution of standard Cs solutions, was  $\pm 0.2$  ppm.

In the thermodynamic analysis, samples consisting of 10.00 mL of 30.0 mM CsTPB(PC), 10.00 mL of 30.0 mM  $\text{NaNO}_3(\text{aq})$ , and 5.00 mL of TPA were shaken together and held in an ice bath. Samples were removed from the ice bath, allowed to warm to a measured temperature, and then shaken again. Upon separation, an aliquot of the PC phase was taken.

$K_{\text{Cs}}$ , the extent of reaction for Cs in the sample, was calculated as  $[\text{Cs}]_{\text{init}} - [\text{Cs}]_{\text{final}} / [\text{Cs}]_{\text{final}}$  from the concentration of Cs in the PC phase, as determined by FES. The state variables were then determined by  $-RT \ln K = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ .

## Results and Discussion

**Solubilities and pH Effects of System Components in Pure Phases.** The three-phase liquid separation is easy to perform physically because the three liquids quickly separate into distinct layers, with PC on the bottom, excess TPA on the top, and the aqueous Cs-containing solution as the middle layer. However, the system is complicated by the fact that all three solvents are miscible to some degree in each other. TPA is soluble in water to about 15 mM, while PC is soluble to about 1 M concentration in water. As might be expected, both Cs and Na are soluble in PC as MTPB and in water as  $\text{MNO}_3$ . NaTPB is soluble in water, while CsTPB is not (see Table 2), and neither nitrate salt is soluble in PC.

The pH of the aqueous phase depends on the number of components in the mixture. (See Table 3.) The addition of a PC phase does not cause a large change in pH. The addition of TPA causes the largest pH change through the formation of tripropylammonium ions ( $\text{H-TPA}^+$ ) and  $\text{OH}^-$ . When both CsTPB and  $\text{NaNO}_3$  are present, the pH of the aqueous phase in the three-phase

**Table 3. pH of Various Combinations of the Three-Phase System**

mL of H <sub>2</sub> O	mol of PC	mol of TPA	mol of NaNO <sub>3</sub>	mol of CsTPB	pH
10.0					6.53
10.0	1.16 × 10 <sup>-1</sup>				6.57
10.0		3.20 × 10 <sup>-2</sup>			10.68
10.0	1.16 × 10 <sup>-1</sup>	3.20 × 10 <sup>-2</sup>			8.53
10.0			5.00 × 10 <sup>-3</sup>		5.83
10.0	1.16 × 10 <sup>-1</sup>		5.00 × 10 <sup>-3</sup>		6.91
10.0	1.16 × 10 <sup>-1</sup>	3.20 × 10 <sup>-2</sup>	5.00 × 10 <sup>-3</sup>		8.10
10.0	1.16 × 10 <sup>-1</sup>	3.20 × 10 <sup>-2</sup>		3.20 × 10 <sup>-4</sup>	7.76
10.0	1.16 × 10 <sup>-1</sup>	3.20 × 10 <sup>-2</sup>	5.00 × 10 <sup>-3</sup>	3.20 × 10 <sup>-4</sup>	7.94
10.0	1.16 × 10 <sup>-1</sup>		5.00 × 10 <sup>-3</sup>	3.20 × 10 <sup>-4</sup>	6.79

system equilibrates at 7.9. At this pH, 99.8% of the TPA in the aqueous phase is present as H-TPA<sup>+</sup>.

**Drivers for the Separation of Cs<sup>+</sup> into the Aqueous Phase.** At first glance, it may appear strange that the proposed process first precipitates Cs<sup>+</sup> from an aqueous phase and then, using many of the same components of the first extraction, exchanges Cs<sup>+</sup> back into an aqueous solution. The reasons for the return of Cs<sup>+</sup> to the aqueous phase in the three-phase extraction involve both reversible ion-exchange equilibria and irreversible chemical reactions.

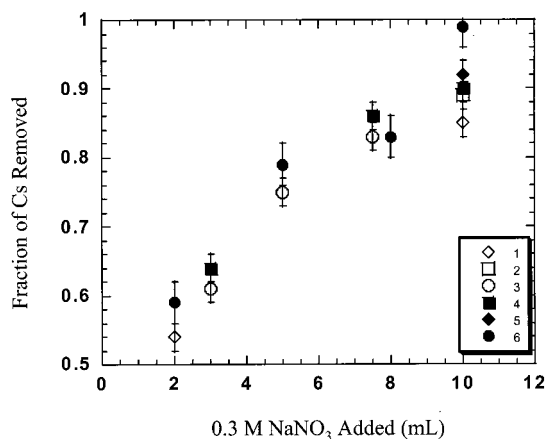
From Figure 2, it can be seen that the addition of either aqueous NaNO<sub>3</sub> or TPA to the system will increase the extraction of Cs<sup>+</sup>, with the addition of the aqueous solution having the major effect. TPA also aids in boosting the fraction extracted, but this has a much smaller effect.

The temperature dependence of the equilibrium constant for three-phase separation shows that the process is entropy-driven (see Figure 3). The equation for the line in Figure 3, which corresponds to the standard free energy for the overall separation of cesium in the three-phase system, is

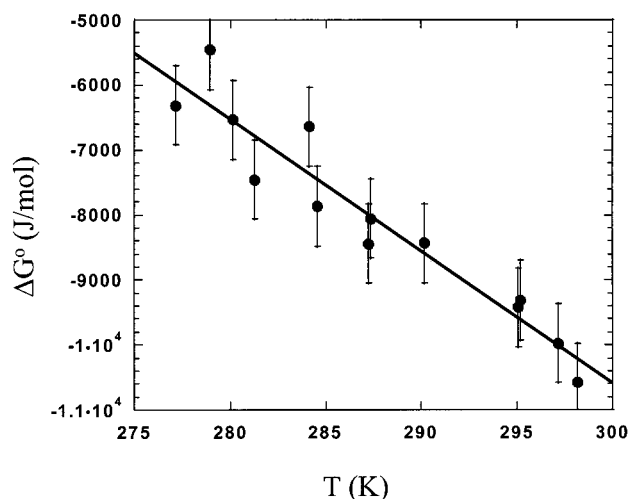
$$\Delta G^\circ = 5047 \text{ J/mol} - 203.6 \text{ J/mol}\cdot\text{K}(TR^2) = 0.912 \quad (1)$$

In the operable range between the freezing and boiling points of water, increasing entropy spontaneously drives the cesium cation into the aqueous phase. This increase in entropy is brought about by the differences in solvation of the Na<sup>+</sup> and Cs<sup>+</sup> ions in the two phases. Na<sup>+</sup>, which has a smaller ionic radius than Cs<sup>+</sup>, has a larger hydration sphere (because the solvent-ordering electric field on the surface of a sphere of radius  $r$  is proportional to  $z/r^2$ ). The difference in hydration is evident in the limiting molar conductivities of the nitrate salts in water. The conductivities of NaTPB and CsTPB are, however, comparable in PC. Cesium cations have a slightly higher conductivity in PC solution, indicating a slightly more mobile, slightly less solvated ion (see Table 2). Thus, the major effect of the exchange of Cs<sup>+</sup> for Na<sup>+</sup> is the disordering of a number of water molecules that were previously confined to the Na<sup>+</sup> hydration sphere. This increase in entropy drives the extraction of Cs<sup>+</sup> into an aqueous NaNO<sub>3</sub> solution. Because  $\Delta H^\circ$  is positive, the Cs exchange is more complete at higher temperature. The fraction of Cs remaining in the PC phase decreases from 0.17 at 3 °C to 0.017 at 24 °C.

The exchange of TPA is chemical in nature and is entwined with the hydrolysis of PC. PC hydrolyzes to form propylene glycol and carbonic acid. The bicarbonate anion, HCO<sub>3</sub><sup>-</sup>, that results from the dissociation of



**Figure 2.** Fraction of cesium removed from 10 mL of 0.035 M CsTPB in PC. Plot objects are numbered by milliliters of TPA added to the mixture.

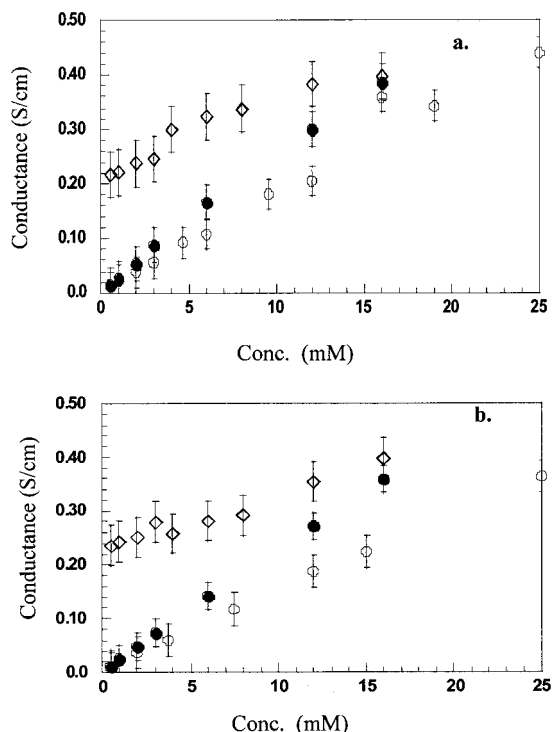


**Figure 3.**  $\Delta G^\circ$  versus temperature for mixtures of 10.0 mL of 0.030 M CsTPB in PC, 10.0 mL of 0.030 M NaNO<sub>3</sub> in H<sub>2</sub>O, and 5.0 mL of TPA. Mixtures were shaken at designated temperatures and allowed to separate. The PC portion was extracted and tested by AES for the remaining Cs concentration in order to determine  $K$ .

carbonic acid is soluble in water and sparingly soluble in PC. The carbonic acid buffers the aqueous solution and has two effects in the ternary liquid mixture. (See Table 3.)

In the absence of TPB, it provides an exchange mechanism for the H-TPA<sup>+</sup> out of the aqueous solution and into the PC phase. This can be clearly seen in conductivity plots of the solutions composing the three-phase mixture. (See Figure 4.) For CsTPB or NaTPB, there is no residual conductivity, beyond that of the solvents themselves, at zero concentrations in the mono- or biphasic systems. However, in the ternary mixtures, conductivity measurements begin at greater than zero for zero concentrations of NaTPB and CsTPB and remain at higher values than those obtained for the less complex systems. This nonzero conductivity demonstrates the presence of additional ions in the PC phase of the three-phase mixture, and these ions only occur when TPA is present in the system.

In the ternary mixture, all aromatic moieties are retained in the PC phase. (See Figure 5.) In addition, the TPB ion is stable in the PC phase, as can be seen by NMR of the aromatics present in the PC. The phenyl groups remain bound to boron as evidenced by the

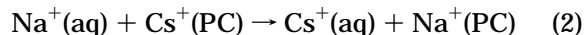


**Figure 4.** (a) Conductance of CsTPB in solvent mixtures: open circles, CsTPB in PC; filled circles, CsTPB in PC/H<sub>2</sub>O; diamonds, CsTPB in PC/H<sub>2</sub>O/TPA. (b) Conductance of NaTPB in solvent mixtures: open circles, NaTPB in PC; filled circles, NaTPB in PC saturated with H<sub>2</sub>O; diamonds, NaTPB in PC saturated with H<sub>2</sub>O and TPA.

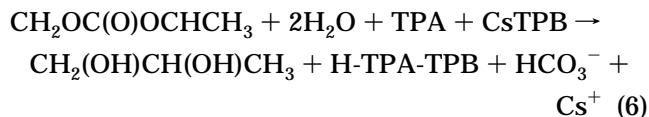
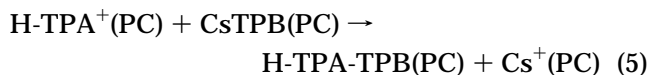
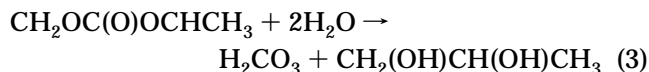
broadened peak at 7.59 ppm. The broadening is caused by the quadrupolar resonance of boron. The areas of the three peaks correspond to a 2:2:1 ratio for the peaks centered at 7.59, 7.22, and 7.07 ppm, respectively. If benzene were present as a decomposition product, it

would be seen in the NMR as a single sharp peak rather than the grouping of two triplets and a broad singlet that are observed. The aromatic-containing compound present in the PC phase is thought to be H-TPA<sup>+</sup>TPB<sup>-</sup>, which ordinarily would precipitate in aqueous solution.

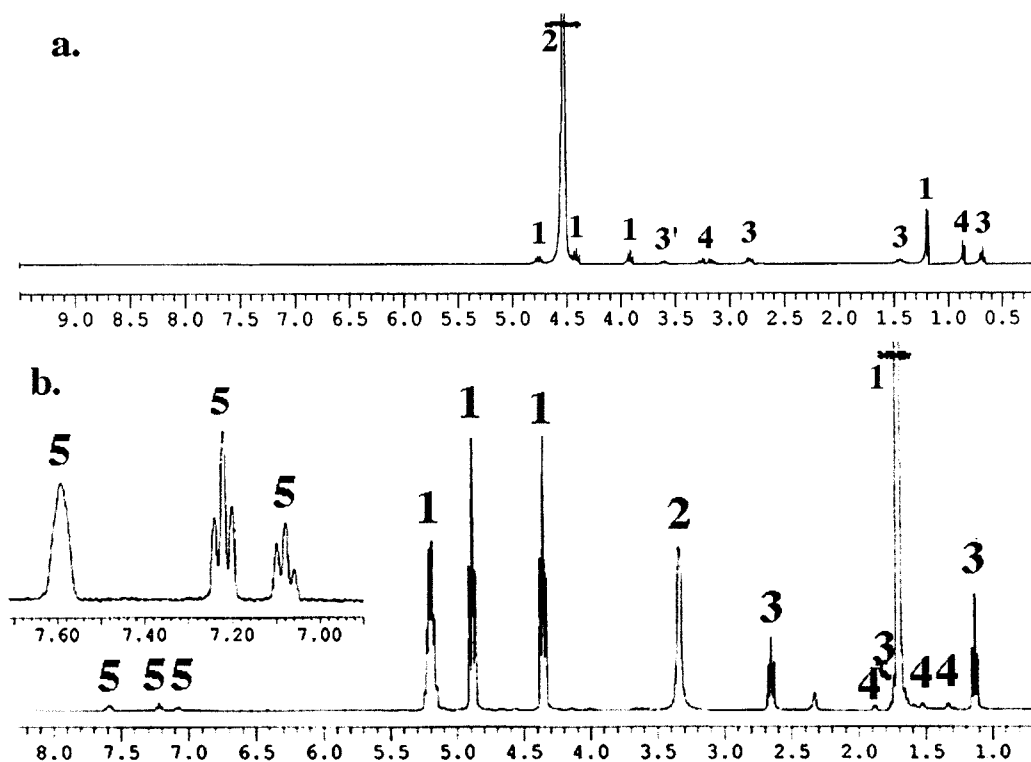
Thus, there are two reactions in the three-phase system which exchange the Cs<sup>+</sup> into the water phase, while maintaining the TPB anion in the PC phase. The primary reaction (2) is entropically driven and is the



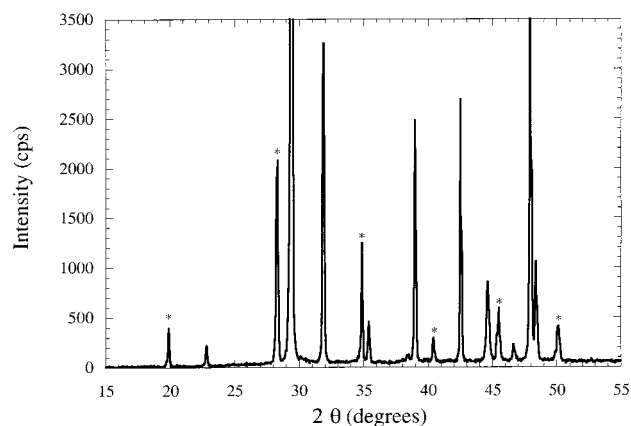
main mechanism for exchange of the cesium into the aqueous phase. The other reaction sequence (3)–(6)



is chemical in nature and provides a means of fixing the TPB in the PC phase while freeing the Cs<sup>+</sup> for phase exchange. The overall result of these two mechanisms is that cesium can be recovered in the aqueous phase while the TPB remains in the organic phase. In tests of a simplified system initially containing 10.00 mL of 1.0 mM NaNO<sub>3</sub>(aq), 10.00 mL of 1.0 mM CsTPB(PC), and 5.00 mL of TPA, recovery of cesium was ≥99.8% in the



**Figure 5.** <sup>1</sup>H NMR spectra of (a) the aqueous phase of the three-phase separation and (b) the PC phase of three-phase separation. Peaks assigned: 1, PC; 2, water; 3, H-TPA<sup>+</sup>; 3', TPA; 4, propylene glycol; 5, TPB<sup>-</sup>.



**Figure 6.** XRD of solids in an evaporated aqueous phase of three-phase separation using  $\text{NaNO}_3(\text{aq})$  and  $\text{CsTPB}(\text{PC})$ . Peaks were indexed to rhombohedral  $\text{NaNO}_3$  (unmarked)<sup>13</sup> and hexagonal  $\text{CsNO}_3$  (\*).<sup>14</sup>

aqueous phase. At these concentrations, 0.2% is the detection limit for cesium using AES.

The targeted removal fraction for the SRS waste is 0.999 99 of the cesium in the bulk stream. This was already accomplished for the bulk waste by the precipitation process using NaTPB. The question remains whether a similar efficiency of separation can be attained in the three-phase extraction method. Because of the detection limits of AES, a radiotracer study, which can provide much lower limits of detection, is needed. However, it should be noted that 99.8% of  $\text{Cs}^+$  is recovered when initial ion concentrations are equal at 1.0 mM. In practice, the initial aqueous sodium concentration is expected to be 3.5–10 M, while CsTPB solubility in PC is limited to about 0.035 M. With a disparity of more than 2 orders of magnitude in the initial concentrations of the alkali-metal ions, it is reasonable to expect a substantially greater separation efficiency than 99.8% because of the ion-exchange equilibrium in reaction (2).

Finally, the disposition of the recovered cesium is of interest. Evaporation of the aqueous phase from the simplified system described above shows that  $\text{Cs}^+$  is recovered as solid  $\text{CsNO}_3$  mixed with  $\text{NaNO}_3$ . (See Figure 6.) In a more complex test, the solids were recovered from precipitation from the SRS simulant, dried, and then rehydrated using the simulant filtrate to form a 10 wt % slurry. A total of 10.00 mL of this slurry was shaken with 10.00 mL of PC and 5.00 mL of TPA. The aqueous phase was then extracted and evaporated to dryness. Because the simulant has orders of magnitude higher concentration of potassium and sodium than cesium, Cs was not detected by XRD in these dried solids. AES measurements were similarly confounded by interference from K and Na in the simulated Cs recovery. Again, radiotracer tests are needed to determine the extraction process in the presence of large amounts of potassium and sodium salts.

**Foaming during Filtration.** While a continuous-flow process of countercurrent mixing followed by rapid filtration can prevent the contamination by benzene of much of the bulk stream, the technical problems of foaming in the filter unit and the final separation and disposal of Cs remain. The foaming, at least in simulated SRS waste (see Table 1), is caused by the addition of NaTPB in greater than stoichiometric amounts to the bulk stream.

Noticeable foaming occurs with the addition of 2.5 times the stoichiometric amount of NaTPB (0.038 M, to precipitate both KTPB and CsTPB) to the simulant. Because the simulant does not contain any particles of metal or metallic catalysts, we believe that this foaming is solely due to excess NaTPB. Adding stoichiometric amounts of NaTPB (0.0151 M), either as a solid or in aqueous solution, to the simulant does not cause foaming.

Introduction of 100 mL of 0.38 M aqueous NaTPB to 1.000 L of the simulant immediately forms an opaque, white suspension that is easily filtered. Addition of 0.038 mol of solid NaTPB to the simulant creates a suspension of fine particles which are difficult to filter, as might be expected from a chemical situation that favors crystal nucleation, and a distinctly different, white, fluffy precipitate that floats on the surface of the liquid. XRD analysis of this low-density solid revealed it to be NaTPB. The high sodium content of the simulant (5.6 M) interferes with the solubility of NaTPB through the common ion effect. Plant engineers report a solubility of 0.2 mM for NaTPB in the Cs waste slurry.<sup>2</sup> Thus, solid NaTPB is expected to be present in the treated bulk waste stream, in amounts far greater than expected in a pure water solvent.

Because CsTPB precipitation is optimal under cold, acidic conditions and the process stream is far from these conditions, the addition of superstoichiometric amounts of NaTPB seems prudent. However, foaming is the inevitable result of adding excess NaTPB. One means of reducing the foaming action could be to add water after the precipitation process. However, this step would greatly increase the total stream volume. A second, more viable, option is the addition of a defoamer or deemulsifying agent. At least one such defoamer has been proposed.<sup>12</sup> A third option is to add NaTPB in a more dilute (<0.020 M), aqueous form. While this method would also increase the total volume of the bulk stream, the resultant ease of filtration may be a satisfactory tradeoff. Further investigation on this point seems warranted.

## Conclusions

In this study, cesium was quantitatively recovered (to the limits of detection) as the aqueous nitrate salt by a three-phase liquid separation. There are two main actions in this process that work to separate the Cs from TPB and exchange the Cs into the aqueous phase. One action is chemical in nature. TPA is protonated in the three-phase system and associates with the TPB in the PC phase. At the same time,  $\text{CsHCO}_3$ , which is only sparingly soluble in PC, is formed. The other action is thermodynamic in nature. The entropy gained by releasing water molecules bound in the larger  $\text{Na}^+$  hydration sphere creates the driving force for the exchange of  $\text{Cs}^+$  from PC to the aqueous phase.

There remain three issues to be resolved in the treatment of the SRS waste. Recovery of only 99.8% of <sup>137</sup>Cs is unacceptably low. However, this figure represents the limit of detection (300 ppb for Cs) for the FES equipment used in this study. A test of the process using radioactive <sup>137</sup>Cs or using ICP-MS, which can allow much lower limits of detection, is needed. We expect that, by using initial concentrations of aqueous sodium at least 2 orders of magnitude higher than the initial concentration of cesium in PC, the exchange reaction

can be driven to higher levels of Cs recovery in the aqueous phase.

The second issue concerns the use of TPA in the process. The original impetus for the suspension of ITP at SRS was the release of a volatile organic into the atmosphere above the tanks. While TPA is not as volatile as benzene (33 °C flash point and 156 °C boiling point for TPA versus -11 °C flash point and 80 °C boiling point for benzene), it is still considered a flammable liquid. There are several points to be considered regarding this issue.

First, there is the difference in bulk waste processing. The generation of benzene in the bulk waste is not the same as application of TPA to a separated slurry. In the former case, the entire waste stream is contaminated. In the latter, the bulk waste can proceed to further processing.

Additionally, TPA can be easily recovered from the organic phases of the three-phase system. Excess TPA remains as the top layer of the separation, while TPA can easily be distilled from the PC (the boiling point of PC is 240 °C). TPA can also be removed from the aqueous phase by evaporation, leaving solid nitrate salts as the product. Whether an evaporation process is desirable depends on the subsequent process steps. If processing of the aqueous phase entails further dilution into a large stream, it may not be necessary to resort to evaporation. During the final vitrification step, the concentration of TPA, which initially is less than 15 mM in the aqueous phase of the separation, would be low enough to have no material effect on the vitrification process.

Finally, the analytical method used in this study did not provide a limit of detection low enough to definitively show remediation of the SRS simulant. The inclusion of potassium into the three-phase separation introduces interferences in the FES measurements because KTPB dissolves in the ternary mixture. Even if extraction of Cs into the aqueous phase is complete, CsNO<sub>3</sub> is too small a component of the product solids to detect by XRD. Thus, it cannot yet be concluded that the proposed process can remediate Cs from the SRS stream. On the basis of extrapolations from simplified systems, nearly complete exchange of Cs into the aqueous phase can be expected. Radiotracer testing using either simulant or actual waste should provide accurate results.

Overall, the proposed process scheme is intended to allow the remediation of Cs by precipitation with NaTPB to proceed at SRS. Rapid separation of CsTPB from the bulk stream by continuous-flow processing

avoids contamination of the bulk stream. The three-phase liquid extraction should allow the rapid separation of the Cs from TPB (and TPB from the caustic aqueous solution) to circumvent the means of decomposition for the slurry. After Cs is extracted back into the aqueous phase, the slurry should be ready for immediate inclusion in a HAW stream for final disposal.

### Acknowledgment

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