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EVALUATION OF 1-HYDROXYETHANE-1,1-DIPHOSPHONIC ACID AND SODIUM CARBONATE AS STRIPPING AGENTS FOR THE REMOVAL OF Am(III) AND Pu(IV) FROM TRUEX PROCESS SOLVENT

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ABSTRACT

The TRUEX solvent extraction process is being developed for the removal of the transuranic (TRU) elements from some of the wastes stored in tanks at the U.S. Department of Energy's Hanford Site. Initial flowsheets for this process call for the stripping (back extraction) of TRUs with 0.2 M 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) followed by washing of the process solvent with 0.25 M sodium carbonate. The stripped TRU stream is to be neutralized with caustic for interim storage in carbon steel tanks prior to vitrification. Such a scenario would result in a considerable amount of phosphorus and sodium in the TRU stream, which could preclude this material from being efficiently vitrified in the proposed Hanford Waste Vitrification Plant (HWVP). An examination of alternative stripping processes suggests that the amount of phosphorus and sodium in the feed to HWVP can be reduced by 1) using a less concentrated solution of HEDPA in the strip step, or 2) using sodium carbonate as the stripping agent. The latter approach would eliminate the introduction of phosphate into the TRU waste stream. It would also greatly simplify the process by combining the strip and solvent wash steps. Furthermore, less caustic would be required to prepare vitrification feed streams for interim storage. A third approach involving the use of a combined sodium carbonate/NaHEDPA solution to strip the TRUs also shows promise. The distribution behaviors of Am(III) and Pu(IV) between HEDPA solutions or sodium

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carbonate solutions and TRUEX solvent have been examined. Results of stripping experiments using solutions prepared from both spiked and actual Hanford tank wastes are presented in this paper.

INTRODUCTION

The Transuranic Extraction (TRUEX) process (1,2) is being developed for the treatment of selected radioactive wastes stored in underground tanks at the U.S. Department of Energy's Hanford Site. Figure 1 is a flowsheet of the proposed treatment. This process involves the extraction of transuranic elements from nitric acid solutions with a solvent consisting of 0.2 M octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) plus 1.4 M tributylphosphate (TBP) in a normal paraffin hydrocarbon (NPH) diluent. After passing through a suitable scrub step,[2] the transuranic (TRU) elements are stripped from the extract. The solvent passes through a solvent wash step (0.25 M Na_2CO_3) and is then recycled to the extraction stage.

Two waste streams result from this process. The raffinate from the extraction contactor will contain little enough TRU material that it can be classified as low-level waste (LLW), which can be cast in grout and stored in near-surface vaults. The aqueous phase from the strip contactor contains most of the TRUs, and thus (along with any undissolved residue) must be classified as high-level waste (HLW). The HLW will be vitrified in borosilicate glass for ultimate disposal in a deep geologic repository. Because the volume of the resulting HLW stream is much less than the volume of the original waste, a large cost saving is achieved by running this process (as compared to vitrifying the waste directly).

Initial flowsheets for the treatment of Hanford tank wastes specified the use of a 0.2 M 1-hydroxyethane-1,1-diphosphonic acid

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[2] The scrub solutions used may be a function of the type of waste being processed.

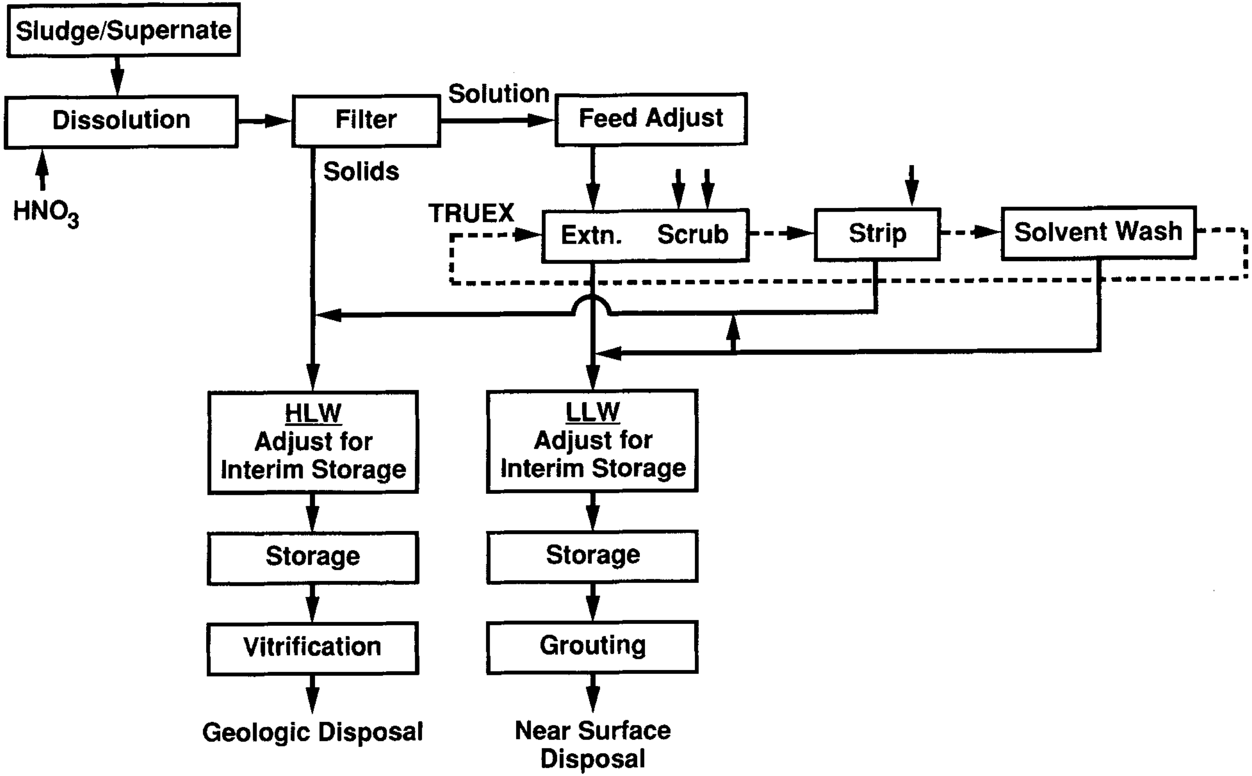

FIGURE 1. Generic flowsheet for the treatment of Hanford tank wastes by the TRUEX process.

(HEDPA) solution to strip the TRUs from the extract. HEDPA has been shown to form strong complexes with Eu(III) in acid solution (3), and the utility of this compound in stripping TRUs from the TRUEX process solvent has been demonstrated (4). The use of HEDPA as the stripping agent will result in the addition of phosphorus into the HLW stream, and thus into the feed to the vitrification plant. This has raised some concerns that the amount of phosphorus present would become the limiting factor in the number of glass canisters that would be required to dispose of these wastes (thus reducing the economic incentive to use the TRUEX process).

This paper presents the results of a study aimed at reducing the amount of phosphorus introduced into the HLW stream. Three approaches have been investigated: 1) Reduction of the concentration of HEDPA in the strip solution; 2) use of carbonate as stripping agent; and 3) use of a strip solution containing both sodium carbonate and NaHEDPA (the sodium salt of HEDPA).

EXPERIMENTAL

General. The TRUEX process solvent (0.2 M CMPO + 1.4 M TBP in NPH) was provided by Westinghouse Hanford Company, Richland, Washington. The solvent was washed with three successive 0.5 volumes of 0.25 M Na_2CO_3, then twice with 0.5 volumes of deionized water. 1-Hydroxyethane-1,1-diphosphonic acid was obtained from Albright and Wilson Americas as a 60% solution and was used as received. Diluted stock solutions of HEDPA were analyzed by titration with standard NaOH.

Tracer Distribution Measurements. The HEDPA stripping experiments were performed by mixing appropriate amounts of stock 1 M HNO_3, 0.2 M HEDPA, and deionized water. The solutions were spiked with either Pu(IV)[3] or Am(III) tracer and shaken with an equal

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[3] The oxidation state of the plutonium tracer was confirmed to be +4 by extraction with thenoyltrifluoroacetone (5).

volume of TRUEX solvent at ambient temperature for 60 s. After centrifugation, samples from each phase were withdrawn for liquid scintillation counting. The counting was achieved by mixing the samples in OPTI-FLUOR™ liquid scintillation cocktail (Packard Instrument Co., Downers Grove, Illinois) and counting on a Packard Tri-Carb® 4000 Liquid Scintillation Counter. The distribution coefficients were calculated as the concentration of Am or Pu in the organic phase divided by the concentration of Am or Pu in the aqueous phase.

For the carbonate strip experiments, the TRUEX solvent was first contacted with an aqueous nitric acid solution (0.05 M), which had been spiked with either Pu(IV) or Am(III). The resulting organic extract was then contacted with 0.25 M Na_2CO_3 at an organic-to-aqueous phase ratio of 1.

The distribution behavior of nitric acid was determined by potentiometric titration of samples from both phases with standard NaOH. These measurements were made under conditions identical to those used for the Am(III) distribution measurements.

RESULTS AND DISCUSSION

Stripping with HEDPA

Distribution coefficients (D) for the extraction of Am(III) and Pu(IV) from HEDPA solutions with TRUEX process solvent (0.2 M CMPO + 1.4 M TBP in NPH) have been determined as a function of HEDPA concentration and nitric acid concentration. Figure 2 shows the distribution coefficients for Am(III) and Pu(IV) as a function of HEDPA concentration at an aqueous acidity of 0.35 M HNO_3. The distribution coefficients for both of these ions decreases with increasing HEDPA concentration. The distribution coefficients for Am(III) are generally one order of magnitude greater than those for Pu(IV) under similar conditions. These observations are consistent with those reported by Horwitz et al. (4) The lower distribution coefficients for Pu(IV) indicate that this ion can be stripped from

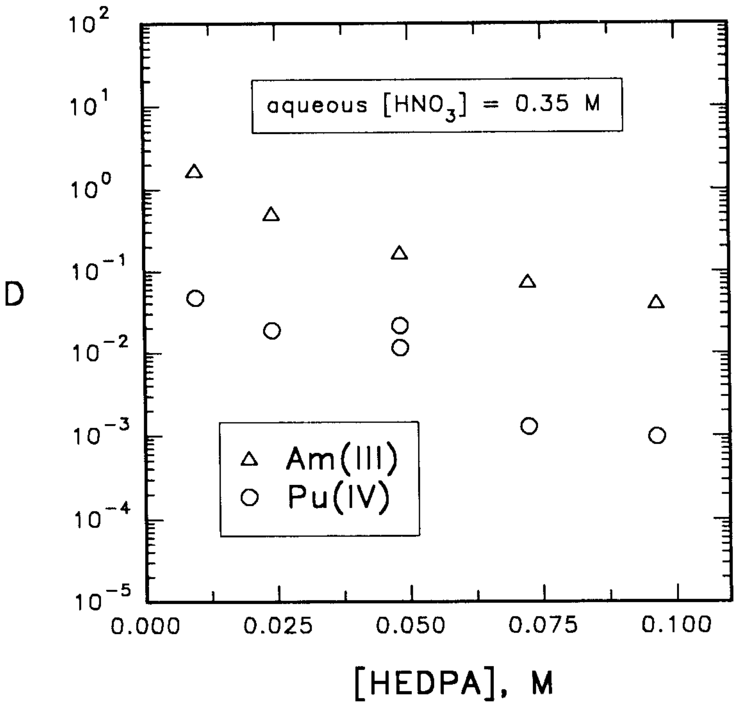

FIGURE 2. Distribution of Am(III) and Pu(IV) between aqueous HEDPA solutions and TRUEX process solvent (0.2 M CMPO + 1.4 M TBP in NPH).

the TRUEX process solvent with HEDPA more readily than can Am(III). Because Am(III) will be the limiting species in the efficiency of the HEDPA strip, subsequent efforts were focused on the stripping of this ion from the TRUEX process solvent.

The distribution coefficients for Am(III) between the TRUEX process solvent and HEDPA solutions as a function of HEDPA concentration and nitric acid concentration are plotted in Figure 3. In this figure, the symbols represent the experimental results and the lines are drawn based on the correlation discussed in the following paragraphs.

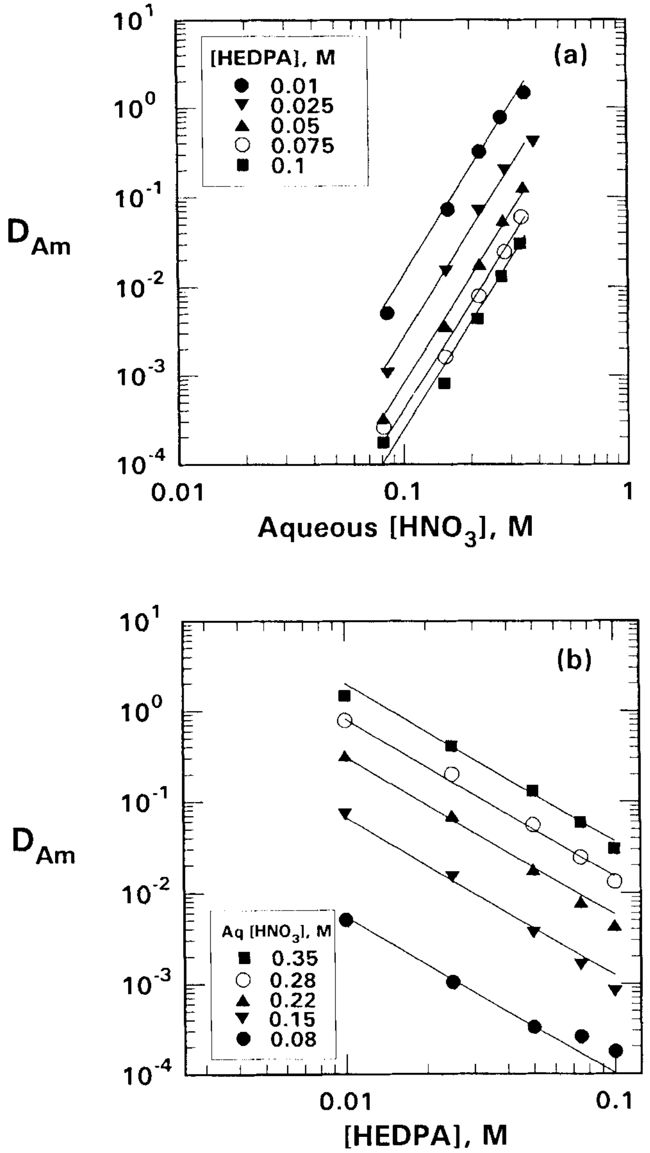

FIGURE 3. Distribution of americium(III) between aqueous HEDPA solutions and TRUEX process solvent (0.2 M CMPO + 1.4 M TBP in normal paraffin hydrocarbon) as a function of (a) concentration of HNO_3 in the aqueous phase at equilibrium and (b) concentration of HEDPA. The solid lines represent distribution coefficients for americium(III) that were calculated using Eq. 1.

The plot of D_{Am} vs. $[HNO_3]$ in the aqueous phase (Figure 3a) reveals a fourth-order dependence of D_{Am} on the aqueous nitric acid concentration; whereas, the plot of D_{Am} vs. [HEDPA] (Figure 3b) indicates that D_{Am} is inversely proportional to the square of the HEDPA concentration. Thus, an empirical model for the calculation of D_{Am} can be developed based on the following equation:

$$D_{Am}=\frac{k[HNO_3]^4}{[HEDPA]^2} \qquad (1)$$

where k is an empirical constant.

The empirical constant k is truly constant only for a given concentration of HEDPA. The values of k for the five different concentrations of HEDPA used here were determined from the Am(III) distribution data plotted in Figure 3 ($k=D_{Am}\bullet[HEDPA]^2\bullet[HNO_3]^{-4}$). The values of k are plotted as a function of [HEDPA] in Figure 4. A linear (logarithmic) relationship exists between k and [HEDPA]; thus, k can be determined for a given concentration of HEDPA that might be considered as a TRUEX stripping solution.

The distribution of nitric acid between HEDPA solutions and the TRUEX solvent is summarized in Figure 5. The distribution of nitric acid is independent of the HEDPA concentration; however, the distribution in the presence of HEDPA does appear to be higher than that observed in the absence of HEDPA (Figure 5, and Ref. 1). For the purposes of the empirical model used to calculate D_{Am}, the solid line depicted in Figure 5 is used. This line was generated by linear regression on all the data points determined in the presence of HEDPA (regardless of [HEDPA]).

For any given set of input HEDPA and HNO_3 concentrations, and a given organic-to-aqueous phase ratio, the distribution coefficient for Am(III) can be calculated from Equation 1 and Figures 4 and 5. Such calculations were carried out for the conditions under which the tracer experiments were conducted, and the results are displayed as the solid lines in Figure 3. As can be seen, the calculated

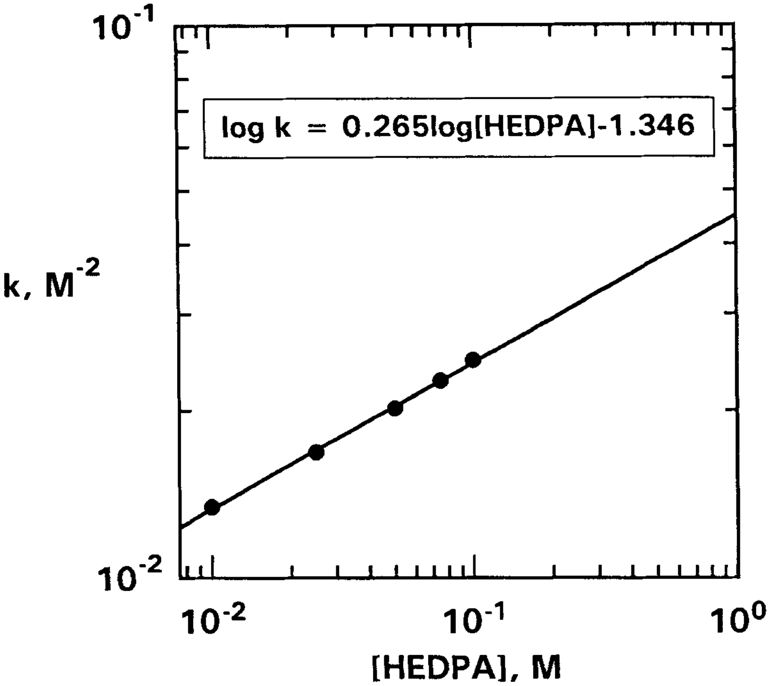

FIGURE 4. The empirical constant k as a function of HEDPA concentration.

values closely agree with the experimental values. The sum of the square of the residuals is 0.29.

The empirical model described above can be used to predict the stripping efficiency of HEDPA solutions under a given set of conditions. The results of several such calculations are presented in Figure 6. For the purpose of these calculations, it was assumed that the strip step involved four successive batch contacts at an organic-to-aqueous phase ratio of 3.00. Three HEDPA concentrations were considered (0.025, 0.05, and 0.1 M), and the residual concentration of nitric acid in the extract coming from the scrub step was assumed to be either 0.5 or 0.2 M. It can be seen from

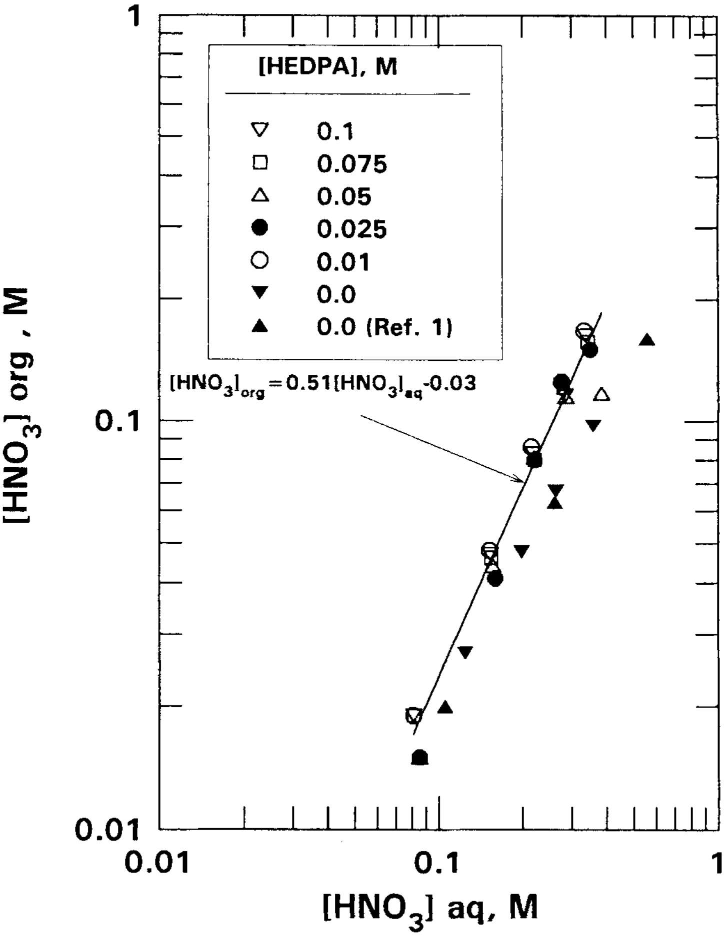

FIGURE 5. The distribution behavior of nitric acid in the TRUEX process.

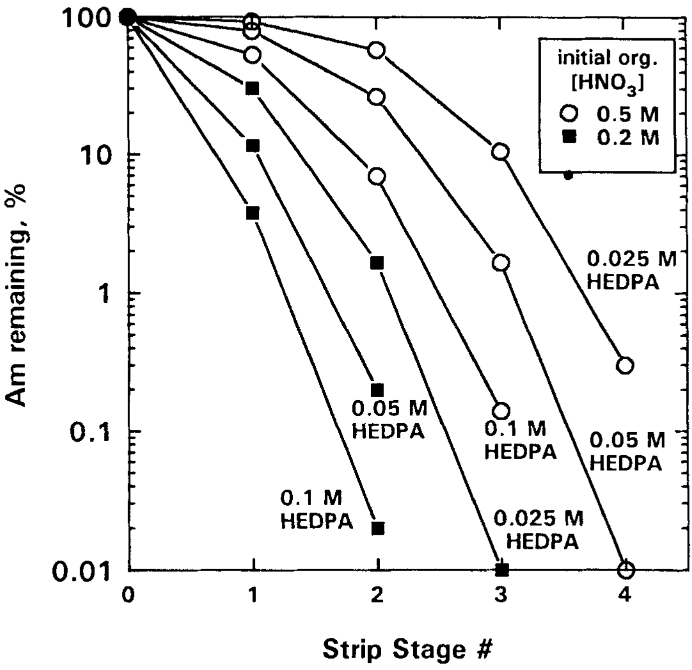

FIGURE 6. Removal of Am(III) from TRUEX process solvent with HEDPA as calculated by Eq 1. The organic-to-aqueous phase ratio is assumed to be 3.0; each strip stage is assumed to be a simple batch contact.

Figure 6 that very efficient stripping of Am can be achieved at low HEDPA concentrations. For example, if the initial concentration of HNO_3 in the organic phase is 0.2 M, two contacts with 0.1 M HEDPA results in the removal of greater than 99.9% of the Am. However, by adding one more stage, this level of stripping can be exceeded with 0.025 M HEDPA. Figure 6 illustrates the importance of scrubbing HNO_3 from the extract prior to the strip step. For all HEDPA concentrations, markedly better stripping efficiencies are achieved when the initial organic nitric acid concentration is 0.2 M rather than 0.5 M. This is a result of the fourth-order dependence of D_{Am} on the nitric acid concentration (Figure 3, Equation 1).

An experiment was recently performed in our laboratory to assess the effectiveness of the TRUEX process in the treatment of an actual Hanford tank waste (6). The sludge waste used in this investigation resulted from the chemical process used to remove the Zircaloy cladding from N Reactor fuel, and it is referred to as neutralized cladding removal waste (NCRW). The bulk components of NCRW sludge are zirconium hydroxide and sodium fluoride. The TRU content is on the order of 1000 nCi/g. The experiment was designed to simulate the counter-current TRUEX solvent extraction processing of acid-dissolved NCRW waste. The results of this experiment are reported elsewhere (6); however, the results of the stripping steps are relevant to this work and will be discussed here.

The scrubbed NCRW extract was contacted with a 0.21 M solution of HEDPA at an organic-to-aqueous phase ratio of 3.00. Two subsequent strip steps were done with fresh 0.21 M HEDPA at the same organic-to-aqueous phase ratio to ensure removal of the TRUs for mass-balance calculations. The aqueous phase nitric acid concentration in the first strip step was 0.36 M. Using Equation 1 (and a k value determined from Figure 4), a value of 0.011 was predicted for D_{Am} in this step. The value determined experimentally for D_{Am} was 0.020. Better agreement between the calculated and experimental values was obtained when the concentration of uranium in the waste sample was taken into account.

The uranium concentration in the aqueous phase from the first strip step was 0.034 M. If each uranium binds two HEDPA ligands, the effective HEDPA concentration for the stripping of TRUs would be 0.14 M, and the predicted D_{Am} would be 0.023. The latter value is within experimental error of the experimental value. Thus, the model developed from the tracer data was found to accurately predict the distribution behavior of Am in an actual waste.

In another series of experiments with actual waste, a scrubbed TRUEX extract (containing approximately 0.02 M HNO_3) from a dissolved NCRW solution was divided into several aliquots, each of which was contacted with a different strip solution (organic-to-aqueous phase ratio = 1). Four of these strip solutions contained only HEDPA at concentrations ranging from 0.2 to 0.01 M. The concentrations of alpha-emitting nuclides in 0.1, 0.05, and 0.01 M HEDPA strip solutions were respectively 104, 104, and 90% of the concentration found in the 0.2 M HEDPA strip solution. These results provide additional, albeit less definitive, support that effective stripping of TRU elements from extracts of real Hanford wastes can be achieved at HEDPA concentrations much below 0.2 M.

Stripping with Sodium Carbonate

As an alternative to using HEDPA as the stripping agent for the Hanford TRUEX process, we explored the possibility of using sodium carbonate solutions to strip the TRUs from the solvent. Stripping with sodium carbonate would have several advantages over the use of HEDPA. Use of a sodium carbonate strip would eliminate the addition of phosphorus into the HLW waste stream. Because the sodium carbonate could be used to perform another needed function (neutralization of process acids before interim storage in carbon steel tanks), no extra sodium would be added to the HLW stream. Furthermore, the overall process would be simplified by combining the strip and solvent wash steps (Figure 1).

Tracer experiments were carried out in which 0.25 M Na_2CO_3 solutions were contacted with an equal volume of TRUEX solvent that had been spiked with Pu(IV) or Am(III). D_{Am} was found to be 0.001 and D_{Pu} was 0.009. This result suggested that sodium carbonate would be an effective stripping agent. However, an experiment with an actual NCRW extract was less encouraging. When a TRUEX extract of real NCRW ($[HNO_3]$ in the extract = 0.15 M) was contacted with a 0.5 M sodium carbonate solution (organic-to-aqueous phase ratio of 3.00), a precipitate formed in the aqueous phase. This precipitate was found to be rich in lanthanum. The distribution coefficient for the total alpha activity was 0.2. Thus, with NCRW extract, the performance of sodium carbonate as a stripping agent was not as efficient as expected from tracer experiments. Furthermore, the quantity of lanthanum present in this type of waste would cause precipitation problems in the contactor if carbonate is used to strip the TRUs.

Combined Sodium Carbonate/NaHEDPA Strip

A third approach to the stripping of the transuranic elements from the TRUEX process solvent is now being considered. This approach involves using a strip solution that contains both NaHEDPA (the sodium salt of HEDPA) and sodium carbonate. The effectiveness of such solutions for removing TRUs from the solvent has been compared to the effectiveness of HEDPA solutions alone. Aliquots of the scrubbed extract (containing approximately 0.02 M HNO_3) discussed above were contacted with NaHEDPA and Na_2CO_3 mixtures (organic-to-aqueous phase ratio = 1) to compare their stripping effectiveness with those of the various HEDPA solutions. The concentration of alpha-emitting nuclides in a 0.01 M NaHEDPA + 0.25 M Na_2CO_3 strip solution was 104% of that found in the 0.01 M HEDPA strip solution, while the concentration in a 0.002 M NaHEDPA + 0.25 M Na_2CO_3 strip was 107% of that in the 0.01 M HEDPA strip solution. The 0.002 M NaHEDPA strip solution represented a 100-fold decrease in the amount of phosphorus in the strip solution (as compared to the 0.2 M HEDPA currently specified in Hanford TRUEX process flowsheets). No precipitation was observed in these NaHEDPA/Na_2CO_3 strips, but the concentration of lanthanum present in the feed solution was much less than that present in the experiment in which precipitation was observed with the carbonate alone strip (1.4×10^{-5} M compared to 6.5×10^{-4} M). Thus, it could not be determined from this experiment whether NaHEDPA will prevent lanthanum from precipitating in the presence of carbonate. However, these results are encouraging, and this area warrants further study.

SUMMARY

1-Hydroxyethane-1,1-diphosphonic acid is a very efficient reagent for the stripping of transuranic elements from the TRUEX

process solvent. An equation was derived from the experimental data which can be used to predict the Am distribution coefficients between HEDPA solutions and TRUEX process solvent. Sodium carbonate shows promise as a stripping reagent, but in the processing of Hanford NCRW sludge, complexants such as HEDPA must be added to prevent lanthanum precipitation. Combined NaHEDPA/Na_2CO_3 strip solutions are effective at removing the TRUs from the solvent.

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