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RECOVERY OF PLUTONIUM AND AMERICIUM FROM CHLORIDE SALT WASTES BY SOLVENT EXTRACTION*

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ABSTRACT

Plutonium and americium can be recovered from aqueous waste solutions containing a mixture of HCl and chloride salt wastes by the coupling of two solvent extraction systems: tributyl phosphate (TBP) in tetrachloroethylene (TCE) and octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) in TCE. In the flowsheet developed, the salt wastes are dissolved in HCl, the Pu(III) is oxidized to the IV state with NaClO₂ and recovered in the TBP-TCE cycle, and the Am is then removed from the resultant raffinate by the CMPO-TCE cycle. The consequences of the feed solution composition and extraction behavior of these species on the process flowsheet design, the Pu-product purity, and the decontamination of the aqueous raffinate from transuranic elements are discussed.

INTRODUCTION

Chloride salt wastes, which contain non-negligible amounts of Pu and, in some cases, Am, need to be made discardable due to their ever-increasing volumes and the limited amount of storage space (1). The objectives of this work were to develop a solvent

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Table 1. Approximate Composition of DOR, ER, and MSE Salt Wastes

DOR ^a		ER ^b		MSE ^c	
Salt	wt%	Salt	wt%	Salt	wt%
CaCl ₂	90	NaCl	39	NaCl	22
CaO	9	KCl	51	KCl	28
Ca(metal)	1.2	PuCl ₃	10	MgCl ₂	30
Pu(metal)	0.09-0.3			Pu	19
				Am	0.8

^aComposition given in (3).

^bComposition given in (2).

^cComposition calculated from data given in (4).

extraction process for chloride salt wastes that would 1) recover the Pu and remove other transuranic elements; 2) produce a Pu product containing <1000 ppm total of other metals, with none exceeding 100 ppm; and 3) produce an aqueous waste yielding <100 nCi of alpha activity per gram of solid. Chosen to accomplish these objectives was a two cycle flowsheet in which the first solvent cycle, tributyl phosphate (TBP) in tetrachloroethylene (TCE), recovers the Pu and the second solvent cycle, octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) in TCE, removes the Am and other transuranic elements.

BACKGROUND

Chloride salt wastes are generated from the pyrometallurgical processing of Pu by direct oxide reduction (DOR), electrorefining (ER), and molten salt extraction (MSE). Table 1 lists the approximate compositions of these three categories of salt wastes. The wastes to be processed could either be the chloride salts themselves or wastes generated through the leaching of MgO crucibles or other scraps. As a result, the wastes contain or may contain Pu, Am, Ca, K, Na, Mg, Fe, W, Ta, Ga, Zn, U, Th, and any metals that dissolve out of stainless steel (2).

EXPERIMENTALReagents

For the solvents, tri-n-butyl phosphate (99+%) and TCE (99.9%) were obtained from Aldrich Chemical Co., Inc., and CMPO was obtained from M&T Chemical Co. and purified by the mixed ion exchange procedure of Horwitz et al. (5), which was slightly modified. Reagent grade HCl and metal chloride salts were used to prepare the aqueous solutions. The simulated salt solutions were prepared in three ways: 1) a 1:1 mole ratio of NaCl and KCl with 0, 30, or 70 wt % of MgCl₂ (used as a substitute for MgO) was dissolved in 2M HCl; 2) a 1:1 mole ratio of NaCl and KCl with 30 or 70 wt % MgCl₂ was dissolved in 6M HCl; or 3) CaCl₂ was dissolved in 6M HCl. The sodium chlorite, which was used in the oxidation of Pu(III), was a technical grade (80%) from Aldrich Chemical Co., Inc. Radiotracers used in the distribution ratio measurements were either obtained from Amersham or were from stocks at Argonne National Laboratory.

Reduction of Pu(VI) and Oxidation of Pu(III)

The Pu-chloride/HCl stock solution was prepared from a nitric acid stock solution by adding HCl and boiling the solution to dryness three times. This procedure produced Pu in the VI state, as determined spectrophotometrically with a Perkin-Elmer model 340 spectrophotometer. To reduce the Pu(VI) to Pu(III), a five-fold excess of Fe(II) was added. Upon mixing, the Pu(VI) was converted to the III state within an hour. The presence of Pu(III) was confirmed spectrophotometrically.

The reduced Pu solution, which after reaching equilibrium contained a mixture of the III and IV states (6), was oxidized to the IV state with sodium chlorite (NaClO₂). Unless otherwise noted, a 10:1 chlorite-to-Pu mole ratio was used in the distribution ratio measurements. For the Pu(IV) distribution ratio measurements, the NaClO₂ was added to the aqueous phase just prior to addition of the Pu and temperature equilibration.

Distribution Ratio Measurements

Before the distribution ratio measurements were made, the solvent was pre-treated by a four step process. First, the solvent was scrubbed with 0.25M Na₂CO₃ (O/A=2, where O/A is the organic-to-aqueous phase ratio) to convert acidic impurities into sodium salts that are soluble in the aqueous phase. The solvent was then washed with 0.5M HCl (O/A=2) and filtered through Whatman #1 filter paper. Finally, the solvent was pre-equilibrated with the aqueous phase to be used in the distribution measurements.

The distribution ratio between an organic phase and an aqueous phase containing one of the metal ions, which was at tracer levels except for Mo, was measured after allowing the two phases ($O/A=1$) to temperature equilibrate in a thermostated water bath set at the appropriate temperature for at least five minutes. The two phases were then contacted for 30 to 60 seconds, centrifuged, and separated. Aliquots of the organic and aqueous phases were analyzed by radioanalytical techniques except for Mo, which was determined by Inductively Coupled Plasma (ICP) analysis. For the ICP analysis, the Mo had to be stripped from the organic phase with $0.5M$ HCl before the measurement. Distribution ratio measurements for HCl were conducted in the same manner as for the metals, except that the HCl was stripped from the organic phase with water before it was titrated with standardized NaOH using a Metrohm 636 Titroprocessor. When the distribution ratios were >1 , forward and back extractions were performed to confirm the results.

RESULTS AND DISCUSSION

Extraction by TBP in TCE

Figure 1 shows the distribution ratios of some selected metal ions and HCl as functions of the HCl concentration of the aqueous phase. The distribution ratios (D_{Pu}) for Pu(IV), which agree with results obtained in CCl_4 by Larsen and Seils (7), show that Pu(IV) can be extracted ($D_{Pu} > 10$) from aqueous solutions containing at least $5M$ HCl and it can be stripped ($D_{Pu} < 0.1$) with HCl concentrations as high as $3.5M$. This figure also shows that Pu(IV) can be separated easily from Am and alkali and alkaline earth elements. Calcium, sodium, potassium, and magnesium were all found to have distribution ratios less than 10^{-2} . The separation of Pu(IV) from Th(IV) can also be easily accomplished since the Th(IV) distribution ratios are $< 10^{-2}$ for 1 to $12M$ HCl (8). The separation of Pu(IV) from Zn, W, and Ta, which also have distribution ratios from 10^{-2} to 1 (8), should be possible by loading the solvent with Pu and by scrubbing the solvent with $6M$ HCl. Solvent loading and scrubbing should also help to eliminate U(VI), which has distribution ratios in the range of 1 to 20 in 2 to $8M$ HCl (7), from the loaded organic phase. Separation of Pu from Fe, Ga, and Mo will be difficult since they are well extracted by TBP from acidic chloride media. If Fe or Ga are known to be present at high concentrations, it may be possible to strip the Pu(IV) from the solvent with 3.5 to $4.0M$ HCl and then remove Fe and Ga with lower concentrations of HCl before the solvent is recycled. Another possible method for separating Pu(IV) from Fe and Ga is to extract them from an aqueous phase containing not Pu(IV) but Pu(III), which has distribution ratios $\leq 10^{-2}$ for 1 to $8M$ HCl.

Most of the separations of Pu from other metals depend on Pu being in the IV state, where it has high distribution ratios at

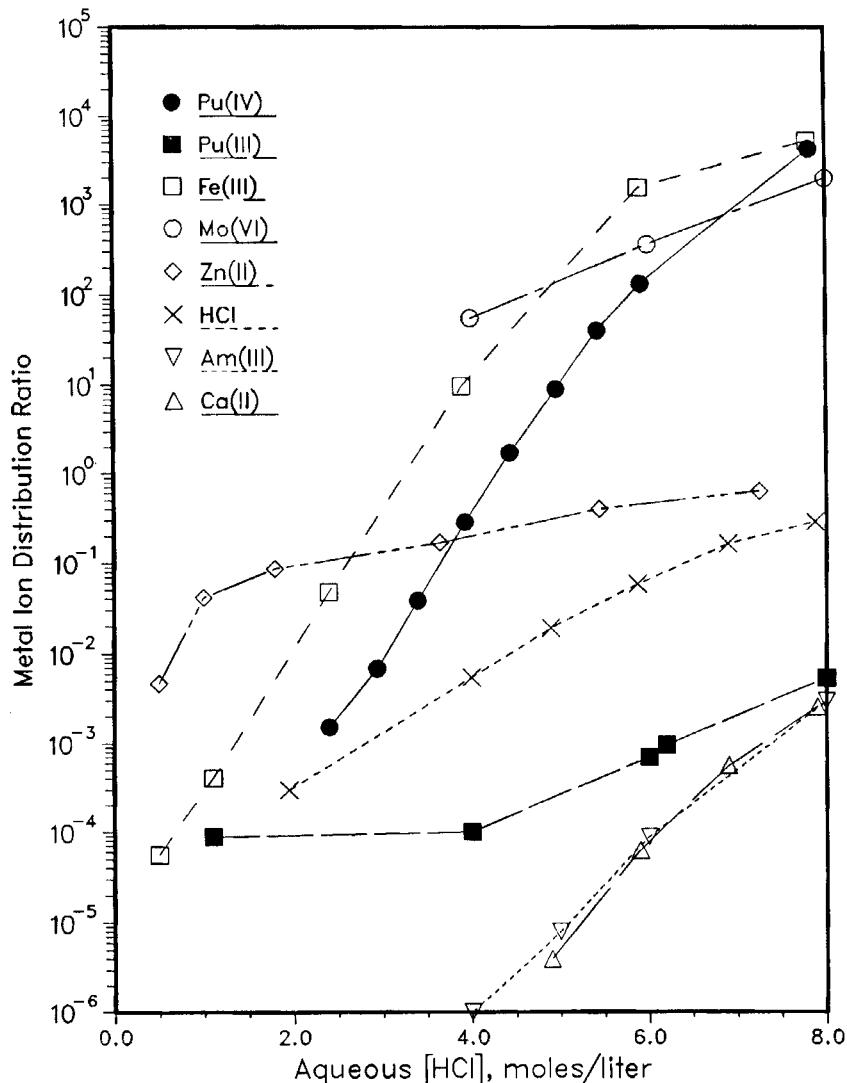


Fig. 1. Metal Ion Extraction by 25 Vol % TBP in TCE from HCl Solutions at 25°C.

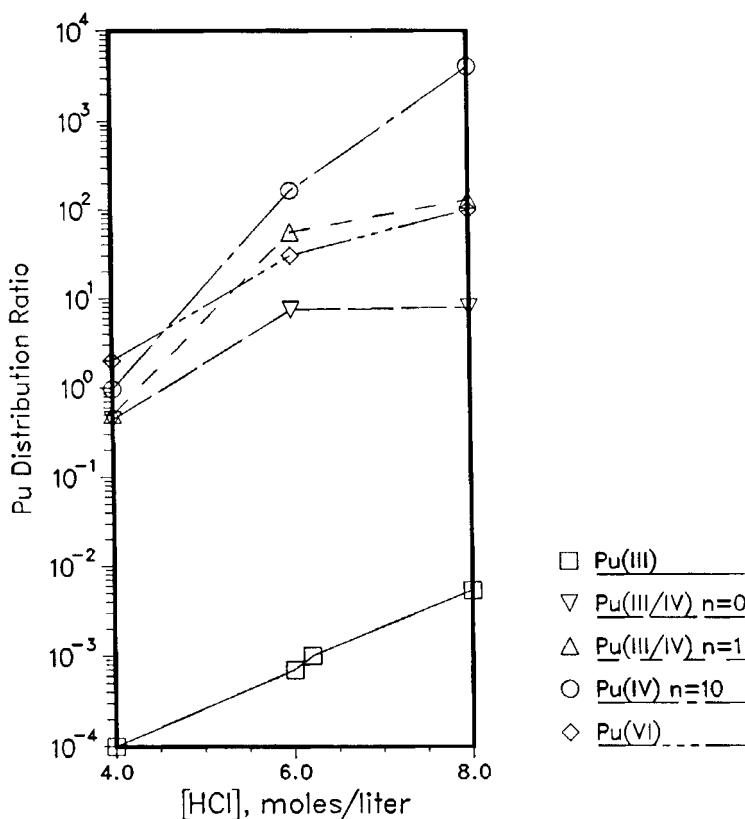
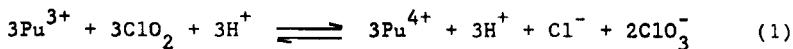


Fig. 2. Plutonium Extraction by 25 Vol % TBP in TCE from HCl Solutions at 25.0°C with $[\text{NaClO}_2] = n[\text{Pu}]$.

high HCl concentrations. However, Pu in acidic chloride solutions exists as a mixture of predominantly the III and IV states (6). Figure 2 shows the wide variation in the Pu distribution ratio results for Pu(III), for mixtures of Pu(III) and Pu(IV), and for Pu(IV). Distribution ratios for Pu(III) were obtained from solutions after reduction of Pu(VI) by Fe(II). The equilibrium results ($n=0$) were measured after allowing a Pu(III) solution to sit at room temperature for six days. More complete and rapid oxidation of Pu(III) was achieved by the addition of various amounts of sodium chlorite to the aqueous phase just prior to extraction. A 1:1 chlorite-to-Pu mole ratio permits 98% of the Pu to be extracted from 6M HCl. This chlorite-to-Pu ratio is probably slightly more than the stoichiometric amount of

chlorite needed to accomplish the oxidation. The stoichiometric amount of chlorite needed is not certain since reduction of chlorite is very complex (9). The actual oxidant is probably not chlorite but chlorine dioxide as suggested by Kanevskii and Fedorova (10) for the oxidation of U(IV) by chlorites. Equation 1 summarizes the oxidation-reduction process that may be occurring in Pu(III) solutions containing chlorite.



The 10:1 chlorite-to-Pu mole ratio results are shown in Fig. 2 as a Pu(IV) reference. This high chlorite-to-Pu mole ratio is probably not achievable at other than tracer conditions due to solubility limitations in concentrated chloride salt solutions. Further, the 10:1 chlorite-to-Pu results also show that Pu is not oxidized to the VI state when an excess of the oxidant is present. The distribution ratios, shown in Fig. 2, for Pu(VI) are lower than those for Pu(IV) by approximately an order of magnitude at 6 and 8M HCl and higher than that for Pu(IV) at 4M HCl by a factor of two.

The dependency of the Pu(IV) distribution ratios on the solvent composition is shown in Fig. 3. The Pu(IV) distribution ratios, which are plotted as a function of the free TBP concentration, yield a straight line with a slope of approximately three. The free TBP concentration was determined to be

$$[\text{TBP}]_{\text{free}} = [\text{TBP}]_{\text{total}} - 3([\text{HCl}]_{\text{org}}) \quad (2)$$

from the dependency of the HCl distribution ratio on the total TBP concentration of the solvent. This dependency was measured between 5.8M HCl solutions and 0.3 to 1.5M TBP in TCE.

The dependency of the Pu(IV) distribution ratios on the aqueous chloride activity of HCl solutions and of acidic chloride solutions simulating dissolved chloride salt wastes is shown in Fig. 4. Aqueous chloride activities for the HCl-only solutions were taken from the literature values (11) for the mean activities of HCl. For the acidic chloride salt solutions, the aqueous chloride activities were calculated (12). The distribution ratios $< 10^3$ yield a straight line with a slope of between five and six. This result indicates that the Pu(IV) distribution ratio can be estimated from the chloride activity of the aqueous phase. The greater than fifth order dependence of the Pu(IV) distribution ratio on the chloride activity of the aqueous phase suggests that species such as HPuCl_5 and H_2PuCl_6 are extracted by TBP. The TBP extraction of H_mMX_n species, where $m=1,2$ and $n=3,4$, has been suggested for Zn from chloride and bromide media (13). Work on fitting these data to a solvent extraction mechanism, which includes Pu complexation by the chloride ion (14), is underway.

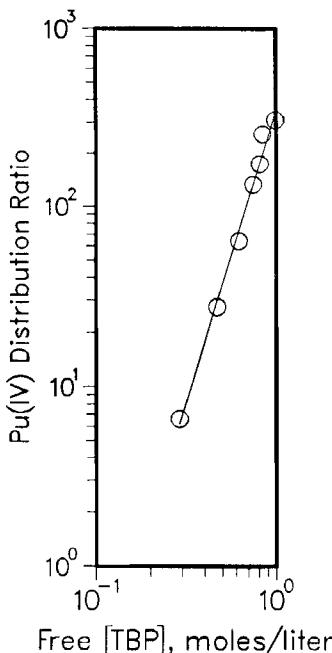
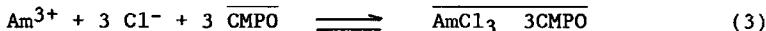


Fig. 3. Pu(IV) Extraction by TBP in TCE from 6M HCl at 25.0°C.

Extraction by CMPO in TCE

Figure 5 shows the dependency of the Am(III) distribution on the aqueous chloride activity of HCl and of acidic chloride solutions, which simulate chloride salt waste solutions. The HCl-only results yield a straight line with a slope of three, in agreement with the expected extraction reaction,



reported by Horwitz et al. (15). Since the Am(III) distribution ratios measured for the acidic chloride solutions fall on or close to the line, the distribution ratios can be estimated from the chloride activity of the aqueous solution. These results show that Am(III) can be extracted ($D > 10$) from an aqueous solution having a chloride activity ≥ 30 , e.g., 6M HCl and stripped ($D \leq 10^{-1}$) with an aqueous solution having a chloride activity < 5 , e.g., 3M HCl. Studies done by Horwitz et al. (16) have further shown that 0.5M CMPO in TCE effectively removes U(VI), Pu(IV), Np(IV), and Th(IV) as well as Am(III), from acidic chloride media.

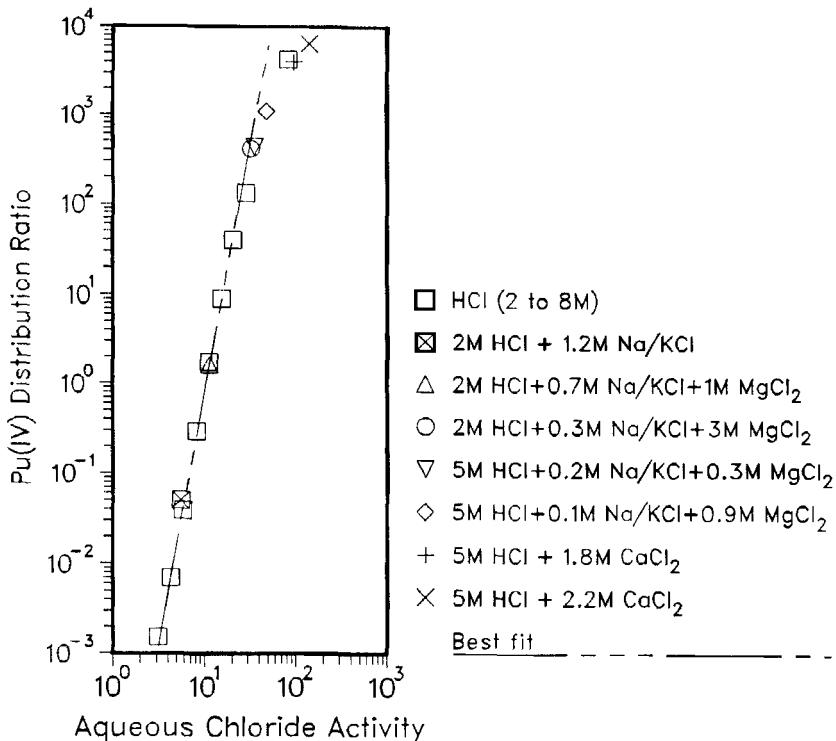


Fig. 4. Pu(IV) Extraction by 25 Vol % TBP in TCE from Acidic Chloride Solutions at 25.0°C.

Flowsheet for Chloride Salt Wastes

Figure 6 is a schematic of the two-cycle process flowsheet. Initially, the chloride salt waste to be processed is dissolved in 6M HCl. The Pu(III) is then oxidized to the IV state by the addition of an aqueous solution of NaClO_2 at a greater than 1:1 chlorite-to-Pu mole ratio. The aqueous feed solution is now ready to enter the extraction stage of the TBP-TCE cycle. After the loaded organic phase is scrubbed with 6M HCl to remove impurities such as Zn, it is stripped of the Pu product with $\leq 3\text{M}$ HCl. If Fe and Ga are suspected of being present at high concentrations, the loaded organic is stripped of the Pu product with 3.5 to 4M HCl. This step will leave the Fe and Ga mostly in the organic phase. The Fe and Ga are stripped out of the organic phase with dilute HCl before the solvent is recycled. An alternative way to achieve a high-purity Pu product from a feed solution containing Fe and Ga is to add a head-end cycle where

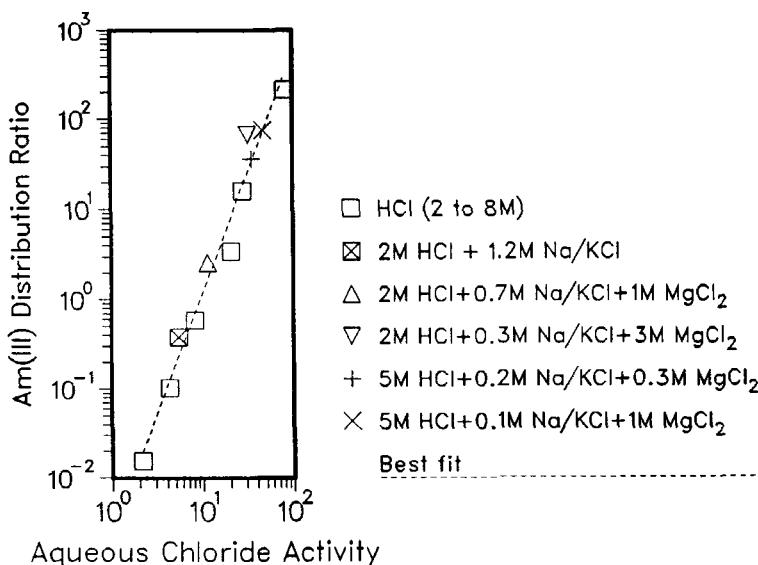


Fig. 5. Am(III) Extraction by 0.5M CMPO in TCE from Acidic Chloride Solutions at 25.0°C.

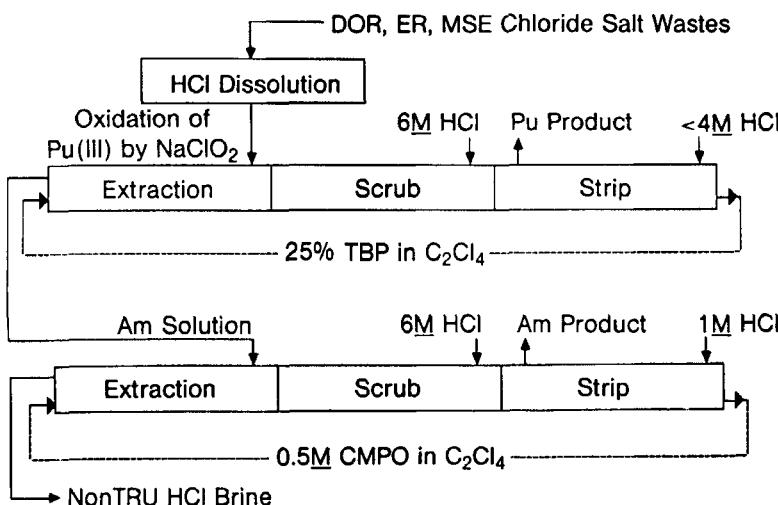


Fig. 6. Process Flowsheet for Acidic Chloride Salt Wastes.

the Fe and Ga are extracted by TBP prior to the oxidation of the Pu(III). The Pu in the raffinate from this head-end cycle is then oxidized and extracted as described above. Cleanup for the TBP solvent is accomplished by scrubbing with 0.25M Na_2CO_3 and filtering it with a discardable filter. Before the solvent is recycled, it may be necessary to add TCE because of losses from evaporation.

The raffinate from the TBP-TCE cycle can be processed by the CMPO-TCE cycle. The chloride activity of the feed solution is adjusted to at least 30 (equivalent to 6M HCl) so that the Am distribution ratio is ≥ 10 when this solution is contacted with the CMPO-TCE. The loaded organic phase is then stripped of Am with 1M HCl, leaving the raffinate with less than 0.01% of the initial Am (based on four extraction stages with O/A = 1). As for the TBP-TCE solvent, addition of TCE will probably be necessary.

One concern in any two-cycle, two-solvent process is the possibility that the two solvents could be accidentally mixed. Although process control is beyond the scope of this paper, the consequences of such occurrences may be predicted. If CMPO-TCE were inadvertently added to the TBP-TCE solvent, the Pu and possibly some or all of the Am would be extracted by this mixed solvent. The Am and some of the Pu would then be removed from the solvent in the dilute HCl strip while the remaining Pu would come out in the carbonate wash. By taking some precautions, such as periodically monitoring the activity of the wash, this sort of error would be found. One possible solution to rectifying such an error would be to recycle both the strip and the carbonate wash from this accident after adding HCl and replacing the mixed solvent with TBP-TCE. On the other hand, the addition of the TBP-TCE to the CMPO-TCE solvent would dilute the CMPO but the Am would still be extracted and stripped accordingly (16).

CONCLUSIONS

From the results, it appears that the proposed two-cycle process can 1) recover Pu and remove other transuranic elements from chloride salt wastes, which have a wide range of compositions; 2) produce a Pu product containing < 1000 ppm total of other metals, with none exceeding 100 ppm; and 3) produce an aqueous raffinate yielding < 100 nCi of alpha activity per gram of solid. The high recovery of Pu results from 1) the nearly complete oxidation of Pu(III) to the IV state, which can be achieved with sodium chlorite in acidic chloride solutions, and 2) the high Pu(IV) distribution ratios between TBP in TCE and acidic chloride solutions. Purity of the Pu product can be enhanced by 1) stripping the Pu with a higher HCl concentration, thus leaving more-extractable impurities in the organic phase, and/or 2) adding a head-end cycle in which the impurities are extracted by TBP before the Pu(III) is oxidized to the IV state.

Americium, any unextracted Pu, and other transuranic elements in the raffinate from the Pu recovery cycle can then be removed by extraction with CMPO in TCE. Part of the flexibility of the proposed flowsheet results from the ability to predict the distribution ratios for Pu(IV) and Am based on the chloride activities of the aqueous phases, which can be calculated from the aqueous phase composition.

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