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SOLVENT EXTRACTION AND RECOVERY OF THE TRANSURANIC ELEMENTS FROM WASTE SOLUTIONS USING THE TRUEX PROCESS

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High-level liquid waste is produced during the processing of irradiated nuclear fuel by the PUREX process. In some cases the treatment of metallurgical scrap to recover the plutonium values also generates a nitric acid waste solution. Both waste solutions contain sufficient concentrations of transuranic elements (mostly ^{241}Am) to require handling and disposal as a TRU waste. This paper describes a recently developed solvent extraction/recovery process called TRUEX (transuranium extraction) which is designed to reduce the TRU concentration in nitric waste solutions to < 100 nCi/g of disposed form [1,2]. (In the USA, non-TRU waste is defined as <100 nCi of TRU/g of disposed form.) The process utilizes PUREX process solvent (TBP in a normal paraffinic hydrocarbon or carbon tetrachloride) modified by a small concentration of octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (abbrev. CMPO). The presence of CMPO enables the modified PUREX process solvent to extract trivalent actinides as well as tetra- and hexavalent actinides. A major feature of the TRUEX process is that it is applicable to waste solutions containing a wide range of nitric acid, salt, and fission product concentrations and at the same time is very compatible with existing liquid-liquid extraction technology as usually practiced in a fuel reprocessing plant.

To date the process has been tested on two different types of synthetic waste solutions. The first solution is a

typical high-level nitric acid waste and the second a typical waste solution generated in metallurgical scrap processing. Compositions of these synthetic wastes are shown in Tables 1 and 2.

Table 1. Typical Composition of Acidic High-Level Waste

Component	Concentration, M	Component	Concentration, M
HNO_3	1.0	Rh	2.5×10^{-4}
		Pd	8.8×10^{-4}
Na	0.20	Ag	3.7×10^{-5}
Al	0.60	Cd	5.0×10^{-5}
Cr	0.015	Te	2.9×10^{-4}
Fe	0.15	Cs	1.2×10^{-3}
Ni	0.007	Ba	8.1×10^{-4}
F^-	0.15	La	6.1×10^{-3}
SO_4^{2-}	0.20	Ce	1.2×10^{-3}
NO_2^-	0.005	Pr	5.7×10^{-4}
		Nd	1.9×10^{-3}
Se	4.2×10^{-5}	Sm	3.9×10^{-4}
Rb	2.6×10^{-4}	Eu	7.5×10^{-5}
Sr	6.2×10^{-4}	Gd	1.2×10^{-5}
Y	3.5×10^{-4}		
Zr	2.6×10^{-3}	U	12-48 mg/L
Mo	2.4×10^{-3}	Np	25-50 mg/L
Tc	1.0×10^{-5}	Pu	0.2-0.4 mg/L
Ru	9.9×10^{-4}	Am	0.005-0.05 mg/L

Table 2. Typical Composition of Plutonium Scrap Waste

Component	Concentration, M	Component	Concentration, M
HNO_3	1.5	Mn	0.003
		Fe	0.03
F	0.09	Ni	4×10^{-4}
		Cu	3×10^{-4}
Be	7×10^{-5}	Zn	6×10^{-4}
Na	0.04	Pb	5×10^{-4}
Mg	0.06		
Al	0.43	U	0.7-700 mg/L
K	0.003	Pu	3-14 mg/L
Ca	0.06	Am	1-3 mg/L
Cr	4×10^{-4}		

Two different TRUEX process solvent compositions are employed depending on the type of waste solution to be processed. TRUEX solvent used for processing high-level liquid waste requires a normal paraffinic hydrocarbon (NPH) diluent with an average carbon chain length of thirteen. Such diluents have flash points of ~ 100°C which is well above the minimum of 80°C that is usually required for PUREX solvent used to process irradiated nuclear fuel. TRUEX process solvent containing 0.2 M CMPO - 1.4 M TBP in Conoco C_{12}-C_{14} has been found to have optimum distribution ratios for americium and high loading capacities without third phase formation (1). (Conoco C_{12}-C_{14} is a commercial NPH containing 12% C_{12}, 56% C_{13}, and 28% C_{14}.) TRUEX solvent used for processing metallurgical scrap waste requires a nonflammable diluent such as carbon tetrachloride or tetrachloroethylene (TCE). Optimum distribution ratios for americium have been obtained with 0.25 M CMPO - 0.75 M TBP in CCl_4 or TCE [3]. Third phase formation does not occur with CCl_4 or TCE diluents even when the solvent is saturated with Am(III) or Pu(IV).

Tables 3 and 4 show the distribution ratios obtained for the major constituents of each waste solution using the appropriate TRUEX process solvent. The phase ratios and temperatures selected for the measurements were chosen to simulate the conditions in the first extraction stage.

Figure 1 shows the generic TRUEX process flowsheet. The process is generic because it is applicable to solutions containing a wide range of nitric acid, fission product, and salt concentrations. For each type of waste solution, the TRUEX process is capable of reducing TRU concentration by many orders of magnitude.

Acidic high-level waste solutions require the addition of oxalic acid to the feed to suppress extraction of Zr and Mo by forming inextractable oxalato complexes. The oxalic acid concentration is generally in the range of 0.15 to 0.25 M depending on the concentration of Al in the waste solution. (High concentrations of Al require high concentrations of oxalic acid.) As the data in Table 3 predict, essentially all of the Am, Pu, and U and a major portion of the Np are extracted (without any oxidation state adjustment) into the TRUEX process solvent. Rare earth fission products and Tc are extracted to varying extents depending on the organic/aqueous phase ratio and the number of extraction

Table 3. Distribution ratios from an acid high-level waste (0.15 M $H_2C_2O_4$)
Organic Phase 0.2 M CMPO - 1.4 M TBP-Conoco C_{12}-C_{14}
O/A = 0.5, T = 40°C

Component	D	Component	D
HNO_3	0.3	Rh	$<10^{-1}$
		Pd	0.4
Na	$<10^{-2}$	Ag	$<10^{-1}$
Al	$<10^{-2}$	Cd	$<10^{-1}$
Cr	$<10^{-2}$	Te	$<10^{-1}$
Fe	0.05	Cs	$<10^{-2}$
Ni	$<10^{-2}$	Ba	$<10^{-2}$
F^-	-	La	4
SO_4^{2-}	-	Ce	6
NO_2^-	-	Pr	6
		Nd	6
Se	$<10^{-2}$	Sm	6
Rb	$<10^{-2}$	Eu	5
Sr	$<10^{-2}$	Gd	4
Y	2		
Zr	0.04	U(VI)	$>10^2$
Mo	0.2	Np(IV), Np(V)	$>10^3$, <0.5
Tc	3	Pu(IV)	$>10^3$
Ru	0.4	Am(III)	7

Table 4. Distribution ratios from a Pu scrap waste solution
Organic Phase 0.25 M CMPO - 0.75 M TBP-CCl_4
O/A = 0.33, T = 30°C

Component	D	Component	D
HNO_3	0.2	Mn	<0.01
		Fe	0.06
F	-	Bu	<0.01
		Cu	<0.01
Be	<0.04	Zn	<0.01
Na	<0.01	Pb	<0.01
Mg	<0..001		
Al	<0.0001	U(VI)	$>10^2$
K	<0.01	Pu(IV)	$>10^3$
Ca	<0.01	Am(III)	17
Cr	<0.001		

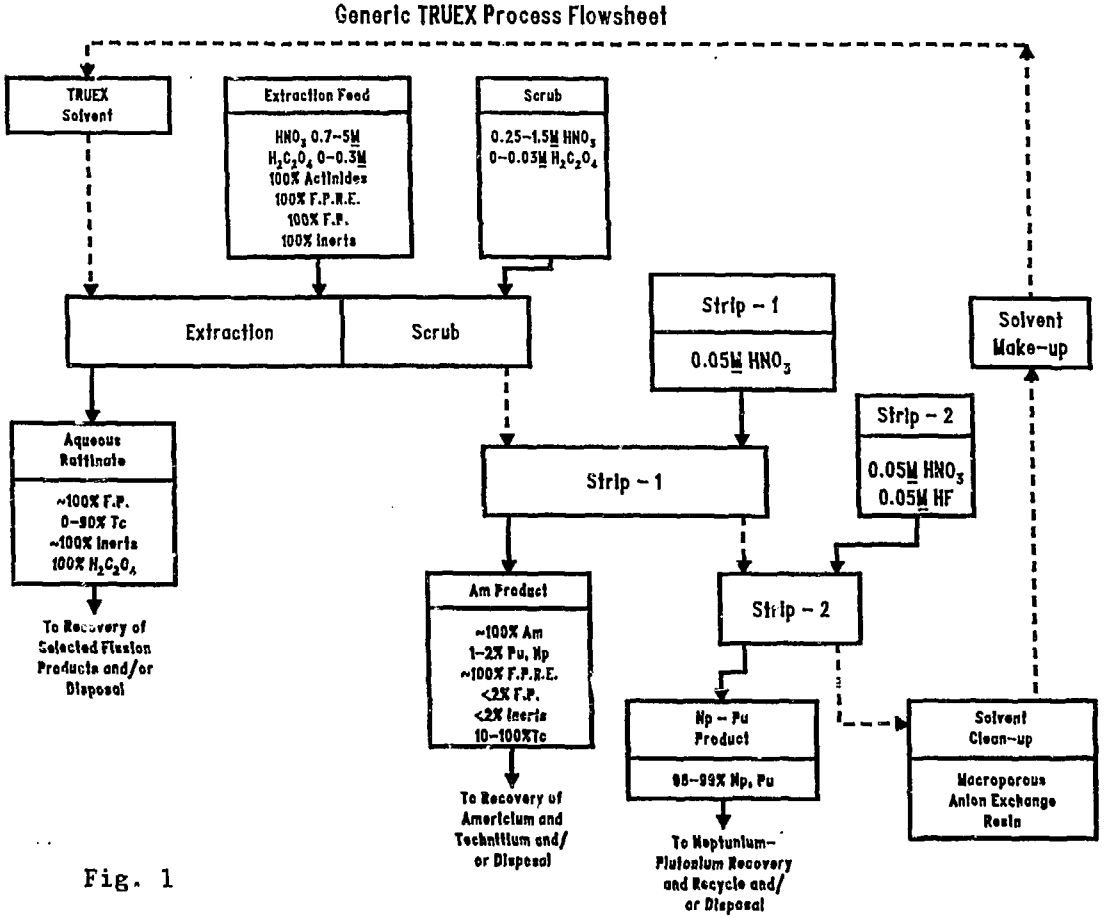

Fig. 1

stages. More than half of the Y and La may be rejected to the aqueous raffinate under proper conditions.

Extensive scrubbing of the organic phase is unnecessary since a few percent of non-rare earth fission products in the Am-rare earth product does not significantly increase the quantity of TRU waste. A small concentration of Fe(III), e.g. 0.005 M, in 0.5 M HNO_3 is used to remove the small quantity of oxalic acid which extracts into the organic solvent. Failure to remove oxalic acid during the scrubbing operation can result in a rare earth oxalate precipitate during stripping operations.

Nitric acid waste solutions generated during the processing of Pu metallurgical scrap require no addition of oxalic acid to the feed. The data in Table 4 for scrap waste show that the only non-actinide constituent with any significant distribution ratio is Fe (D_{Fe} = 0.06). Iron is easily scrubbed from the organic solvent in a few stages using 0.25 M HNO_3.

The stripping sequence of TRUEX process solvent shown in Fig. 1 effectively separates Am from Pu. D_{Am} and the Pu(IV)/Am(III) separation factor from 0.05 M HNO_3 are 0.15 and 10^3, respectively. Since the major fraction of Pu is in the tetravalent oxidation state in nitric acid, only a small quantity of Pu is removed with the Am. A mixture of 0.05 M HNO_3 - 0.05 M HF effectively strips Pu(IV) from the solvent. Under these conditions D_{Pu} = 0.02. Uranyl nitrate is stripped during solvent cleanup operations.

Extensive stripping of the TRU elements from TRUEX solvent is required before spent solvent can be recycled. Efficient stripping of the solvent is dependent on maintaining low concentrations of acidic extractants, which are formed from hydrolysis and radiolysis of the TBP and CMPO. TRUEX process solvent is effectively purified from acidic impurities using a macroreticular anion exchange procedure developed for the cleanup of PUREX process solvent (4). Since TRUEX solvent is essentially PUREX process solvent modified by a small quantity of CMPO, the usual radiolytic and hydrolytic degradation products that are produced in PUREX solvent will also be produced in TRUEX solvent. In addition, degradation products from CMPO and its impurities will also be present. Most of the troublesome degradation products from CMPO arise from impurities. Once these degradation products are removed with the macroreticular resin, TRUEX solvent can be adequately purified by the same Na_2CO_3 scrubbing procedures employed for PUREX process solvent.

Batch countercurrent test runs using a synthetic acidic high-level waste as feed has demonstrated the ability of the TRUEX process to effectively reduce the TRU concentration to < 100 nCi/g of solidified raffinate (2). Eight extraction and four scrub stages were used in the test. Decontamination factors of TRU elements from the waste solution were 5×10^4 (Am), $>>10^5$ (Pu and U), and 6 (Np). These decontamination factors reduced the total TRU activity in the raffinate to 40 nCi/g. The weight of TRU waste was reduced by 150 fold.

Batch extraction tests with synthetic Pu scrap waste reduced the Am and Pu concentrations by $>10^3$ and $>10^4$, respectively, in three extraction and two scrub stages. The process reduced the quantity of TRU waste by 10^3. Selective stripping of Am from Pu from the solvent was also demonstrated.

Continuous countercurrent extraction test runs using the ANL annular centrifugal contactors and synthetic Pu scrap waste are in progress at Argonne National Laboratory. Extensive hydrolytic and radiolytic stability and solvent cleanup testing is also in progress at Argonne.

Listed below is a summary of the major features of the TRUEX process.

1. TRUEX and PUREX have very similar extraction, scrub, strip, and solvent cleanup cycles.
2. TRUEX and PUREX process solvents have similar densities, interfacial tensions, and hydrolytic and radiolytic stabilities.
3. TRUEX process solvent can be prepared from existing PUREX solvent inventory since the quantity of CMPO required is small.
4. TRUEX process solvent will effectively extract actinides in the III, IV, and VI oxidation states; therefore, no oxidation state adjustment is necessary and high decontamination factors of TRU elements from waste are easily achieved.
5. TRUEX requires no acidity adjustment since D_{Am} is not very sensitive to nitric acid concentration in the range of 0.7 to 7 M; therefore, the process is easy to control.
6. TRUEX does not increase the volume of solid waste or create difficult to handle waste streams.

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