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EXPERIMENTAL STUDIES AT THE IDAHO CHEMICAL PROCESSING PLANT ON ACTINIDE PARTITIONING FROM ACIDIC NUCLEAR WASTES

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DISCLAIMER

INTRODUCTION

An important objective of the nuclear industry's waste management plan is the minimization of the quantities of waste contaminated with the very long-lived, transuranic (TRU) elements Pu and Am. Although the mass of these elements is small compared to other components such as fission products, cladding materials and chemical additives their presence requires all wastes to be handled as TRU waste with decay periods of >>1000 years. For the U.S. DOE definition of TRU waste see Ref. 1.

For the past six years an experimental program has been in progress at the Idaho National Engineering Laboratory (INEL) to study the feasability of partioning TRU elements from acidic nuclear waste. Early on in the program our efforts were focused on wastes generated at the Idaho Chemical Processing Plant (ICPP)(2-6). Later we participated in a joint effort with the Oak Ridge National Laboratory (ORNL) to evaluate the application of solvent extraction technology developed for ICPP waste to high-level liquid waste (HLLW) that results from reprocessing light water reactor (LWR) fuel (7-11).

Because waste generated at ICPP is so different from that anticipated from the processing of LWR fuel this paper will review TRU partitioning from each waste separately.

WASTE GENERATED AT ICPP

The Idaho Chemical Processing Plant (ICPP) located at the Idaho National Engineering Laboratory near Idaho Falls, Idaho is a multi-purpose reprocessing facility for DOE fuels containing highly enriched U. Fuels routinely processed at ICPP include stainless-steel-clad fast-reactor fuels, Al-clad test-reactor fuels, and Zr-clad fuels for which the ^{235}U enrichments before burnup vary from 50 to 93%. The stainless-steel-clad fuel is electrolytically dissolved in HNO_3, the Al-clad fuels are dissolved in HNO_3-$Hg(NO_3)_2$, and Zr-clad fuels are dissolved in HF and HNO_3. These multi-headend dissolver solutions provide the feed for a single solvent extraction system which is comprised of a first cycle of TBP extraction followed by two cycles of methyl-isobutyl ketone extraction. The uranyl nitrate product from the extraction system is denitrated in a fluidized bed denitrator to UO_3 for shipment.

The aqueous fission product wastes resulting from the ICPP solvent extraction operations contain small amounts of U and transuranium elements; primarily Np, Pu, and Am with traces of Cm and transcurium isotopes. The safe and effective management of these nuclear wastes has been a primary goal of the ICPP operation for the past 28 years. The major technique for management of this waste has been to store the liquid waste safely for a period not to exceed 5 years, followed by solidification of the waste into a granular oxide and storage in stainless steel bins inside a concrete vault. Prior to calcination, the high- and intermediate-level liquid wastes are stored in doubly-con-

tained, cooled, stainless steel tanks. To date, there is no evidence of corrosion from the acidic wastes stored in these tanks. The HLLW have been solidified on a routine basis in the Waste Calcining Facility (WCF) since December 1963, with a resultant eight- to ten-fold volume reduction factor. To date, this pioneering effort has resulted in approximately 55% of the liquid wastes being converted to solids, with approximately 50,000 cubic feet in storage. Although the projected life of the solids storage bins is at least 500 years, the bins are designed such that retrieval of the wastes for further treatment or transport to a Federal repository might be accomplished whenever desired.

The waste generated at ICPP is different with respect to anticipated commercial processing plant waste for two reasons. First, all of the multi-headend processes result in complete dissolution of the cladding and matrix as well as the fission products and actinide elements; second, the production of transuranium elements in highly enriched fuels is less than in low enrichment/high burnup power fuels. Additionally, the total fission product inventory in the fuel is substantially lower at ICPP as compared to power reactor fuels and consequently, the radioactivity of the resulting waste solutions are very different for these two cases. Thus, the ratio of actinides to total solids in the ICPP waste is significantly less than in currently anticipated commercial wastes. The bulk of the raffinate stored at ICPP has been generated from the processing of Zr- and Al-clad fuel elements. The U recovery process for Zr-clad elements requires the addition of aluminum nitrate as both a salting agent and a complexant for the free fluoride present in the dissolution process. When available, the dissolver solution from Al-clad elements is coprocessed with Zr-clad elements, thus serving the same purpose. Raffinates generated from these campaigns are, therefore, similar. The chemical analyses of a major HLLW tank at ICPP are shown in Table I. Actinide analyses are also given in Table I.

A litre of waste shown in Table I, when calcined, results in the production of $\sim$250 g of total solids.

Separation Requirements

The thrust of the experimental program at ICPP was to find a procedure that would separate TRU elements from high-level first-cycle raffinate (see Table I) and leave behind the cladding elements, salting agents, and the bulk of the fission products. Fission-product lanthanides, because of their similar valence and ionic size, would be expected to follow in nearly any simple separation scheme. Americium is present in ICPP waste as a trivalent ion while Pu is most likely present as both Pu(IV) and Pu(VI). Any separation scheme must be applicable to all these ionic actinide species. Due to an instability of dissolver solution toward the formation of Zr and Al fluorohydrates at lower acid levels, decreasing the acidity before actinide separation is impractical.

Of the many solvent systems we studied for removing actinides from ICPP HLLW, extraction with the bidentate organophosphorus reagents, dibutyl-N,N-diethylcarbamylmethylenephosphonate (DBDECMP) and the dihexyl homologue, DHDECMP, are the most promising. This class of compounds was first synthesized by Siddall in the 1960's (12,13) using the Arbuzov rearrangement. Shown below is the preparation of DHDECMP.

$$(C_6H_{13}O)_3P + ClCH_2\overset{O}{\overset{\|}{C}}-N(C_2H_5)_2 \rightarrow (C_6H_{13}O)_2\overset{O}{\overset{\|}{P}}-CH_2-\overset{O}{\overset{\|}{C}}-N(C_2H_5)_2 + C_6H_{13}Cl$$

Siddall investigated the ability of these compounds to extract Am(III), Ce(III), Pm(III), and HNO_3 from 0.1 to 12M HNO_3 solutions. His favorable results led him to suggest such bidentate extractants could be used to remove trivalent actinides from high-level TBP extraction process waste. This idea was later patented (14). Schulz demonstrated in 1973 that DHDECMP was an effective extractant for Am and Pu from radioactive Hanford generated wastes (15).

We have evaluated both DHDECMP and DBDECMP as actinide extractants from the ICPP wastes. Both reagents were purchased from Wateree Chemical Company, Inc., Lugoff, S.C. on a "custom-synthesis" basis. Due to the ease of purifying the "as-received" DBDECMP, much of our early experimental work was with this compound (2,3). When aqueous solubility measurements indicated DBDECMP to be appreciably soluble (60 g/L) in 0.1M HNO_3 our attention was directed to the use of DHDECMP which exhibits an aqueous solubility similar to TBP (0.4 to 0.5 g/L) (2,16).

DHDECMP Purification, Supply and Toxicity

Technical grade DHDECMP (50% pure) contains unreacted starting materials and many inpurities. This grade of DHDECMP is unsuitable for direct application as an extractant because actinides, once extracted, are poorly stripped. The identification of impurities has been reported previously (4).

We purify litre quantities of DHDECMP by vacuum distillation using a centrifugal molecular still. The fraction distilling at ~0.5 Pa and 120°C is ~86% pure DHDECMP and can be used without further treatment for actinide extraction and stripping studies. Impurities present in this product appear to be innocuous. For the sake of simplicity in making volume percent DHDECMP-solvent dilutions, the stock DHDECMP (86%) was considered to be pure.

Starting with 86% DHDECMP, we have prepared 25 mL of >99% pure DHDECMP by preparative liquid chromatography. The liquid chromatograph used was a Jobin Yvon "Chromatospac-Prep 100", Instruments SA, Inc., Mutechen, N.J. Physical properties studied with purified DHDECMP were density, refractive index, viscosity, U-V, IR and NMR spectra. A detailed description of this work and the resultant

physical properties of DHDECMP have recently been published (7). A limited number of extractions were made using this high purity DHDECMP to demonstrate that DHDECMP is the dominant extracting component in our extraction studies.

We have recently developed a new technique for purifying DHDECMP (17,18). Reaction of 20% crude DHDECMP in hexane with 1M $Hg(NO_3)_2$ at 40°C precipitates $Hg(DHDECMP)NO_3$. DHDECMP, liberated from the precipitate with caustic cyanide, is >95% pure. Hexane is used to dissolve the liberated DHDECMP and is later removed in a rotary evaporator. The procedure is fast, inexpensive and has a high yield (~85%) compared to previous methods. The quality of the purified DHDECMP regarding extractions and stripping of actinides is excellent.

The commercial supply of DHDECMP that is of adequate purity to be used directly for actinide partioning has, until recently, been nonexistent. A new supplier (Bray Oil Co., Los Angeles, California) has entered the marketplace. They have provided ample quantities of vacuum distilled DHDECMP (86% purity) for our pilot plant work. The quality of their product is as good as our "in-house" molecular-distilled DHDECMP.

High purity (>99%) DHDECMP extractant was tested with respect to its ability to induce mutation using Salmonella typhimurium bacteria. These tests were performed by Microbiological Associates using standard techniques to detect mutagens. The results of these tests were negative and suggest that DHDECMP is not mutagenic.

Diluent Effects

Our earlier studies have shown that the extraction of Am from synthetic Zr-Al waste solutions is strongly dependent upon the particular carrier solvent used to dilute the DHDECMP (4). Aromatic solvents proved to be good diluents, the best of the aromatics being branched alkane derivatives. A second organic phase forms when solutions of DHDECMP dissolved in straight chain aliphatic hydrocarbons are contacted with aqueous HNO_3 solutions. Decalin, decahydronaphthalene, proved to be a superior diluent when compared to aromatics; however, when DHDECMP-decalin extractants are contacted with $\geq$3M HNO_3 solutions, a second organic phase forms, Addition of an aromatic modifier such as diisopropyl benzene (DIPB) to a DHDECMP-decalin extractant prevents second organic phase formation even at acidities as high as 6M HNO_3. Much of our early work was with xylene and with diisopropyl benzene diluents. Later, with large quantities of extractant being required for cold pilot-plant testing, we focused on the use of a decalin-DIPB diluent.

Reaction Kinetics

Batch contact studies have shown that both Am(III) and Pu(IV) transfer rapidly at 23 to 25°C between DHDECMP-diluent solutions and

aqueous HNO_3. In all tests conducted, equilibrium was reached in <30 seconds.

Radiolysis, Acid Hydrolysis and Cleanup

The DHDECMP extractant is similar to TBP in that acid hydrolysis and radiolysis lead to the formation of acidic organophosphorus degradation products that are powerful extractants especially for Pu(IV) under low acid stripping conditions. When these species are formed and allowed to accumulate in these extractants, the degradation products prevent stripping. Therefore, these acidic species must be removed, and this is normally accomplished through the use of sodium carbonate scrubbing of the used solvent.

During the more recent pulse column tests (19) sodium carbonate (0.1 M) scrubbing was used to recycle the extractant and the pulse columns were periodically cleaned with Turco-4324 (Turco Products, Division of Purex Corporation, Carson, California, U.S.A.). When the solvent was subjected to long periods of acid loading a sequential treatment with sodium carbonate and A26 resin in the OH^- form (Rohm and Haas Co., Philadelphia, Pennsylvania) was necessary to purify and recycle the extractant.

In summary, the extractant (86% pure) appears to be comparable to TBP (3,5,7,20) in terms of radiolysis and acid hydrolysis stability. The extractant has been contacted with HLLW for up to 16 hours, irradiated with spent fuel elements to 50 watt-hrs/liter, and exposed to excessive radiation doses from extracted Am. In all cases, it has been possible to recycle the extractant while maintaining acceptable stripping characteristics and overall losses. A-26 resin (OH^- form) appears to be an excellent means of removing trace acidic impurities that remain after carbonate washing and is recommended as a solvent polishing step before recycle.

Acidic hydrolysis of DHDECMP does not appear to be a serious problem provided there is not an excessive hold-up period between the extraction-scrub operation and dilute-acid stripping. This problem is further reduced when high quality (>95% pure) extractant is used. We compared the effect of hydrolysis on distilled vs chemically purified DHDECMP where the holdup time between the last high-acid scrub step and stripping was varied for up to 24 hours. For each measurement 20% DHDECMP in 2:1 decalin-DIPB was contacted with an equal volume of synthetic Zr-Al HLLW (containing 2×10^{-3} g/L ^{239}Pu), srubbed twice with one fifth volume of 3M HNO_3 then stored in the dark until stripped with 0.005M HNO_3-0.05M $NH_2OH \cdot HNO_3$(HAN). HAN is used to reduce Pu to the valence (III) state. Results of these tests are shown in Figures II and III. The higher purity solvent is more efficiently stripped and appears less affected by hydrolysis.

Typical Actinide vs HNO_3 Distribution Data

The distribution coefficients have been determined for Cf(III), Cm(III), Am(III), Pu(IV), Pu(VI), Np(IV), Np(VI) and U(VI) between 30% DHDECMP in DIPB and various nitric acid concentrations (7). Results shown in Figure 1 indicate that DHDECMP can extract trivalent as well as tetravalent and hexavalent actinides from moderately concentrated nitric acid. In addition the extractant shows favorable stripping characteristics for valence (III) actinides at low acid concentration.

Extraction Studies with Synthetic Zr-Al HLLW

Batch distribution data have been obtained for the extraction of actinides and key elements between 20% DHDECMP in 2:1 decalin DIPB and synthetic Zr-Al HLLW (5). The effect of scrubbing and stripping was also studied. These results are shown in Table IV. Conditions for these measurements are described in Ref. 5.

For those runs where the element under study was extracted but poorly stripped, the effect of an additional equal volume contact with $0.5\underline{M}Na_2CO_3$-$0.025\underline{M}KCN$ was measured. Palladium, Ru, and Hg are effectively removed with the caustic cyanide strip.

Chemical analyses of Al in the aqueous phase before and after extraction contact confirmed our earlier results with 30 volume % DHDECMP in xylene which indicated low extraction (D_{Al} = 0.0025) (4). To obtain an accurate value for Al would have required activation analysis. This was not felt to be warranted. A measurement of Pu(VI) was not included here because previous studies with other diluents have shown higher distribution for Pu(VI) than for Pu(IV).

Extraction Studies on ICPP High Sodium Waste

Low-level wastes high in sodium content have been collecting at the ICPP for years. Though these wastes represent but a small fraction of the total wastes produced, their cumulative volume is considerable (10^6 gal). the typical composition of high sodium concentration waste is shown in Table V.

We have made equal volume batch extraction measurements on synthetic high sodium concentration waste using 20 volume % DHDECMP in 2:1 decalin-DIPB. Only actinides and a few chemical constituents were examined. Extraction data are shown in Table VI (5).

Actinides are readily extracted from synthetic high sodium concentration waste. With the exception of Hg, no other macro constituent would be expected to follow the actinides in a DHDECMP flowsheet. The high distribution for Pu(IV) is most likely due both to the high $NaNO_3$ concentration and the low fluoride concentration.

Flowsheet

Based on batch extraction, scrub and strip data the flowsheet shown in Figure 2 has been developed. Relative flows are shown in parentheses. Six stages of extraction and two stages of scrubbing should produce TRU-free waste (<10 nCi/g) after calcination. The number of stages for stripping was not determined, but we expect at least six stages would be necessary in each column. The second strip column is felt necessary to remove Pu not stripped in the preceding strip column. This flowsheet does not include a specific Hg removal step. The addition of KCN to the carbonate used in the solvent wash column would cause Hg to report to the solvent wash waste.

Though this flowsheet was developed for Zr-Al high-level waste, it should be adaptable to other waste generated at ICPP.

Mixer-Settler Test

Flowsheet parameters have been tested with actual ICPP waste in a multi-stage miniature mixer-settler. The results of these tests and a complete description of the equipment and flow parameters used have been reported (6). Tables VII and VIII summarize the results of hot runs using Zr-Al HLLW and high sodium waste. Both runs involved continuous countercurrent operation using six stages of extraction with 20 volume % DHDECMP in 2:1 decalin-DIPB and two stages of scrubbing with 3M HNO_3. Analytical analyses of feeds and raffinates clearly indicated that TRU elements were fractionated from major waste constituents such as Al, Zr, Na and F.

We have not yet demonstrated the stripping sections of the flowsheet during hot operations. The following section will describe, however, a mixer-settler run on commercial HLLW where stripping was included.

Cold pilot plant tests described by H. R. Maxey in an earlier paper at this symposium have demonstrated stripping and solvent recycle.

HLLW GENERATED FROM COMMERCIAL LWR PROCESSING

The work on commercial LWR waste was performed as part of the U.S. DOE actinide partioning program coordinated by ORNL and was concluded by a successful minature mixer-settler run using actual Purex first-cycle raffinate that was generated from the dissolution of spent H. B. Robinson reactor fuel at ICPP (7). The goal of the program was to demonstrate an extraction procedure that would result in a combined removal (Purex included) of 99.99% of the Pu, 95% of the Np and 99.9% of the Am from HLLW.

Extractant

The DHDECMP (~86% pure) used in this work was prepared by centrifugal molecular distillation. The solvent used was technical grade DIPB. A solution of 30% DHDECMP in DIPB was used as the extractant in this project.

Batch Distribution Studies

Batch distribution experiments were conducted using synthetic waste whose composition has been previously described (7). The quantities of fission products are based on calculations made by the ORIGEN code for typical LWR fuel irradiated to 33,000 MWd/metric ton, cooled for 160 days before reprocessing (21). Only minor amounts of cladding material are present.

Batch distribution studies were conducted on three modified synthetic waste solutions: oxidize (0.1M $NaNO_2$), reduced (0.01M Fe $(SO_3NH_2)_2$-0.02M HSO_3NH_2), and cadmium modified (3.5M HNO_3-0.156M $Cd(NO_3)_2$-0.0044M $H_2C_2O_2$).

Since cadmium modified waste (CMW) was chosen as the most likely form to be used we discuss here only our work on this waste form.

Batch distribution coefficients for actinides and other key elements between CMW and 30% DHDECMP in DIPB are shown in Table IX. Extraction (o/a = 1) was followed by two scrub contacts (o/a = 5), and five strip contacts (o/a = 1). Scrub and strip compositions are explained in the table.

Conceptual Flowsheet For CMW

The basic flowsheet shown in Figure 2 was used, with some modifications, for actinide partioning of CMW. The extractant is 30% DHDECMP in DIPB and the scrub is 3.5M HNO_3-0.05M $H_2C_2O_4$. A flow ratio of one is used for extractant/feed. A flow ratio of 1.7 is used for extractant/scrub. Extraction factor calculations suggest the decontamination levels desired for waste management purposes could be accomplished by seven ideal countercurrent stages. In theory, a five stage scrub should effectively remove the extractable fission products Zr and Mo. It should also remove approximately 50% of the Tc, 10% of the Ru and Y, and less than 1% of the Pd extract.

Under the flowsheet conditions, the first strip contactor would consist of ten equilibrium stages. This would remove greater than 99% of the extracted lanthanides and transuranics. Only 13% of the U is removed by this strip. The second strip contactor, having four theoretical stages, would remove the remaining U and residual Ce, Am and Pu. After this strip, The extractant would contain a minor amount of Np. The only fission products remaining would be Ru, Tc, and a small amount of Pd.

Miniature Mixer-Settler Run on LWR Waste

Nitric acid was used to dissolve the spent fuel from chopped pieces of a H. B. Robinson fuel element that had a burnup of ~27,000 MWd/metric ton and had been cooled for approximately two years. The dissolution, TBP extraction, and raffinate adjustment is described in detail in Ref. 7. The adjusted HLLW was 3.5M HNO_3-0.156M $Cd(NO_3)_2$-0.0044M $H_2C_2O_4$.

A modified 12 stage minature mixer-settler was used for this experiment. Six stages were used for extraction, two for scrubbing, and four for stripping. Flow rates were 1.0, 0.75, 0.25 and 1.0 mL/min for the extractant, feed, scrub and strip, respectively. For the four stages of stripping, 0.05M HAN was used. A second strip section of dilute oxalic acid (see Figure 2) was not used. A schematic of the mixer-settler is shown in Figure 3.

Approximately six hours were taken to reach equilibrium. The experiment was allowed to run an additional 4-1/2 hours before samples were collected. No problems were observed during the course of the experiments. Phases separated clearly with no interfacial crud apparent. The Pu and Am analysis of the feed, raffinate and strip are shown in Table X.

Assuming no volume changes occurred during processing, the feed decontamination factor (DF) for Am and Pu were 9200 and 209. Theoretically, 96% and 99% of extracted Pu and Am, respectively should strip. Since a dilution occurs in going from feed (0.75 mL/min) to strip (1.0 mL/min), the expected concentrations of Am and Pu in the exiting strip are 74.4 and 43.6 μg/mL, respectively. The experimental values in Table X are higher than these theoretical concentrations. Since flow rates are known to no better than 10%, the expected dilution that occurs between feed and strip would be in error by a similar factor. The discrepancy observed is therefore reasonable. Considering this, stripping of Am and Pu was probably greater than 90% in the four strip stages.

Neptunium analysis of feed and raffinate indicated a DF of 4.7 through the process. Had a nitrite oxidant been used a higher DF would undoubtedly have been realized.

The combined actinide removals from the TBP extractions of the LWR fuel and the subsequent minature mixer-settler experiment on the raffinate from those extractions removed greater than 99.99% of the Pu, greater than 95% of the Np, and greater than 99.9% of the Am. Small fluoride additions to the mixer-settler feed would probably permit further reductions in Pu levels. Partioning experiments with ICPP wastes (this paper) have resulted in Pu residuals as low as 0.1 ng Pu/mL (6). Even lower reductions are considered possible.

REFERENCES

1. DOE Appendix 0511, part 1, No. 23.

2. L. D. McIsaac, J. D. Baker and J. W. Tkachyk, U.S. ERDA Report, ICP-1080 (1975).

3. W. W. Schulz and L. D. McIsaac, "Removal of Actinides from Nuclear Fuel Reprocessing Waste Solutions with Bidentate Organophosphorus Extractants," in Transplutonium 1975, eds. W. Muller and R. Lindner, North Holland Pub. Co., Amserdam, 1976.

4. W. W. Schulz and L. D. McIsaac, U.S. ERDA Report ARH-SA-263, (1977).

5. L. D. McIsaac, J. D. Baker, J. F. Krupa, D. H. Meikrantz, and N. C. Schroeder, "Flowsheet Development Work at the Idaho Chemical Processing Plant for the Partitioning of Actinides from Acidic Nuclear Waste," in Actinide Separations, eds. J. D. Navratil and W. W. Schulz, American Chemical Society Symposium Series 117, 1980.

6. J. D. Baker, L. D. McIsaac, J. F. Krupa, D. H. Meikrantz and N. C. Schroeder, U.S. DOE Report, ICP-1182 Rev. (1979).

7. L. D. McIsaac, J. D. Baker, J. F. Krupa, R. E. LaPointe, D. H. Meikrantz and N. C. Schroeder, U.S.DOE Report, ICP-1180 (1979).

8. D. W. Tedder, B. C. Finney and J. O. Blomeke, "Chemical Processing Facilities for Partitioning Actinides from Nuclear Fuel Cycle Waste Mixtures," paper 3.1, Second Technical Meeting on the Nuclear Transmutation of Actinides, Ispra, Italy (April 21-24, 1980).

9. J. O. Blomeke, A. G. Croff, B. C. Finney and D. W. Tedder, "An Overall Assessment of Actinide Partitioning and Transmutation for Waste Management Purposes." paper 3.5, Second Technical Meeting on the Nuclear Transmutation of Actinides, Ispra, Italy (April 21-24, 1980).

10. A. G. Croff, J. O. Blomeke, B. C. Finney and D. W. Tedder, U. S. DOE Report, ORNL-5566 (in press).

11. D. W. Tedder, B. C. Finney and J. O. Blomeke, U.S. DOE Report, ORNL/TM-6982 (in press).

12. T. H. Siddall, (III), J. Inorg. Nucl. Chem., 25 883 (1963).

13. T. H. Siddall, (III), J. Inorg, Nucl. Chem., 26, 1991 (1964).

14. T. H. Siddall, (III), U. S. Patent 3,243,254, March, 1966.

15. W. W. Schulz, U.S. ERDA Report, ARH-2901 (1973).

16. L. L. Burger and R. C. Forsman, U.S. AEC Report, HW-20936 (1951).

17. L. D. McIsaac, J. F. Krupa and N. C. Schroeder, "Method for Purifying Bidentate Organophosphorus Compounds," Patent Application, U.S. DOE Case No. S-51, 761; ACC-PI-71, April 24, 1980.

18. N. C. Schroeder, L. D. McIsaac and J. F. Krupa, U.S. DOE Report, ENICO-1026 (1980).

19. D. B. Chamberlain, H. R. Maxey, L. D. McIsaac and G. J. McManus, "Removal of Actinides from Nuclear Fuel Reprocessing Wastes using an Organophosphorus Extractant," 88th National Meeting of the Americal Institute of Chemical Engineers, June 8-12, 1980, Philadelphia, Pennsylvania, U.S.A.

20. L. D. McIsaac, U.S. ERDA Report, ICP-1086 (1976).

21. W. D. Bond and R. E. Leuze, U.S. ERDA Report, ORNL-5012 (1975).

TABLE I

TYPICAL COMPOSITION OF ICPP Zr-Al HLLW

Bulk Chemical (M)		Actinides (g/L)	
Acidity (H+)	1.5	^{237}Np	1.2×10^{-5}
Nitrate	2.36	^{238}Pu	$\sim 5 \times 10^{-4}$
Fluoride	3.12	^{239}Pu	1.4×10^{-3}
Aluminum	0.68	^{240}Pu	3.4×10^{-4}
Zirconium	0.44	^{241}Pu	1.5×10^{-4}
Iron	0.005	^{242}Pu	4.8×10^{-5}
Boron	0.22	^{241}Am	4.4×10^{-5}
Mercury	$\sim$0.002	^{243}Am	1.2×10^{-6}

TABLE II

PLUTONIUM STRIPPING FROM 20% DHDECMP* AFTER VARIOUS HOLDUP TIMES.
THREE STRIPS WITH 0.05M HAN (o/a=1).

	Time After Loading (hrs)			
	0	2	8	24
% Pu not Stripped	0.083	0.085	0.12	0.25

*Stock DHDECMP (~86% pure) prepared by distillation.

TABLE III

PLUTONIUM STRIPPING FROM 20% DHDECMP* AFTER VARIOUS HOLDUP TIMES.
THREE STRIPS WITH 0.05M HAN (o/a=1).

	Time After Loading (hrs)			
	0	2	8	24
% Pu not Stripped	0.013	0.012	0.024	0.026

*Stock DHDECMP (>95% pure) prepared by Hg precipitation.

TABLE IV

DHDECMP EXTRACTION-SCRUB-STRIP STUDIES WITH SYNTHETIC Zr-Al HLLW

DISTRIBUTION COEFFICIENTS

Feed Component	Extraction[a] Contact	Scrub[b] Contact	Strip Contacts[c] 1	2	3	4
Am(III)	7.6	3.7	0.21	0.015	0.013	--
Pu(IV)	7.6	3.9	0.20	0.004	0.05	--
Np(V)	0.55	0.16	0.010	--	--	--
U(VI)	55.	34.	2.7	0.22	0.25	0.010
Hg(II)	16.	10.	84.	130.	>200.	>200.
Ce(III)	4.8	4.1	0.28	0.017	0.023	--
Ba(II)	0.015	0.011	--	--	--	--
Cs(I)	0.00040	--	--	--	--	--
Cd(II)	0.014	<0.01	--	--	--	--
Pd(II)	1.9	0.62	0.82	1.4	7.2	17.0
Ru(III,IV)	1.2	0.81	7.4	8.2	14.0	8.4
Tc(VII)	1.4	0.93	2.7	1.0	0.68	0.84
Mo(VI)	0.26	0.20	--	--	--	--
Nb(V)	0.079	0.055	--	--	--	--
Zr(IV)	0.0095	0.016	--	--	--	--
Y(III)	0.36	0.41	0.015	--	--	--
Sr(II)	0.018	0.015	--	--	--	--
H^+	0.2	--	--	--	--	--

[a] Equal vol (o/a=1) contact with 20 vol% DHDECMP in 2:1 Decalin-DIPB

[b] Scrub: 3M HNO_3, o/a=5

[c] Strips 1-3: 0.015M HNO_3-0.05M HAN, o/a=1
Strip 4: 0.005M HNO_3-0.05M $H_2C_2O_4$, o/a=1

TABLE V

TYPICAL COMPOSITION OF HIGH SODIUM CONCENTRATION WASTE

Bulk Chemical	(M)	Actinides (g/L)
Acidity (H^+)	1.4	U $\sim 2 \times 10^{-2}$
Nitrate	4.4	Pu $\sim 1 \times 10^{-3}$
Aluminum	0.50	Am $\sim 1 \times 10^{-5}$
Zirconium	$\sim 1 \times 10^{-4}$	
Mercury	0.0050	
Fluoride	$\sim 6 \times 10^{-4}$	
Sodium	1.7	
Chloride	0.030	
Phosphate	0.020	

TABLE VI

DISTRIBUTION DATA FOR 20% DHDECMP AND HIGH SODIUM CONCENTRATION WASTE

Feed Component	Distribution Coefficient
Am(III)	9.5
Pu(IV)	190.0
U(VI)	140.0
Hg(II)	7.7
Zr(IV)	0.05
H^+	0.43

TABLE VII

TRU REMOVAL FROM Zr-Al HLLW: MINIATURE MIXER-SETTLER RUN

	Am		Pu	
	Mass[a] (ng/mL)	TRU Equivalent[b] (nCi/g)	Mass[a] (ng/mL)	TRU Equivalent[b,c] (nCi/g)
Feed	56.6±0.2	~650	2228±5	~580
Mixer Settler Raffinate	0.333±0.001	~3.8	0.864±0.017	~0.23
Decontamination Factor	170		2500	

[a] Isotopic Composition

^{241}Am-87.11, ^{243}Am-12.89

^{238}Pu-20.15, ^{239}Pu-56.56, ^{240}Pu-14.05, ^{241}Pu-6.93, ^{242}Pu-2.31

[b] 1 L of waste calcines to ~250 g.

[c] TRU equivalents exclude ^{238}Pu and ^{241}Pu.

TABLE VIII

TRU REMOVAL FROM HIGH SODIUM CONCENTRATION WASTE:
MINIATURE MIXER-SETTLER RUN

	Am		Pu	
	Mass[a] (ng/mL)	TRU Equivalent[b] (nCi/g)	Mass[a] (ng/mL)	TRU Equivalent[b,c] (nCi/g)
Feed	16.5±0.2	∿120	1095±10	∿230
Mixer Settler Raffinate	∿0.01	∿0.12	∿0.08	∿0.023
Decontamination Factor	>1000		>10,000	

[a] Isotopic Composition

^{241}Am-92.36, ^{243}Am-7.64

^{238}Pu-5.61, ^{239}Pu-82.85, ^{240}Pu-8.63, ^{241}Pu-2.15, ^{242}Pu-0.76

[b] Assuming 1 L of waste calcines to ∿250 g.

[c] TRU equivalents exclude ^{238}Pu and ^{241}Pu.

TABLE IX

EXTRACTION - SCRUB - STRIP STUDIES WITH SYNTHETIC CADMIUM MODIFIED WASTES[a]

	Distribution Coefficients							
		Scrubs[b]		Strips[c]				
Component	Extraction	1	2	1	2	3	4	5
Am^{+3}	6.4	6.6	--	0.83	0.14	0.19	--	--
Pu^{+4}	438	210	51	1.24	0.15	0.23	0.07	--
U^{+6}	74	83	86	17	3.8	2.4	0.02	0.02
$Np^{+5, +6}$	3.9	5.1	5.8	0.1	0.3	3	3	0.1
Tc^{+7}	1.16	1.01	1.07	7.3	3.7	1.4	0.92	0.41
Mo^{+6}[d]	0.25	0.056	0.036	--	--	--	--	--
Pd^{+2}	0.33	0.28	0.30	1.07	2.0	--	24	0.75
Zr^{+4}	0.95	0.035	0.01	--	--	--	--	--

[a] Waste solution made 0.1 M in $NaNO_2$.

[b] Scrub: 3.5 M HNO_3 - 0.05 M $H_2C_2O_4$.

[c] Strip 1-3: 0.05 M HNO_3 - 0.05 M HAN.

Strip 4: 0.005 M HNO_3 -- 0.05 M $H_2C_2O_4$.

Strip 5: 0.5 M Na_2CO_3.

[d] Mo by gravimetric analysis, all other by radiometric methods.

TABLE X

ANALYSIS OF FEED, RAFFINATE AND STRIP FOR Pu AND Am

Feed		Raffinate*		Strip	
^{241}Am μg/L	^{239}Pu μg/L	^{241}Am μg/L	^{239}Pu μg/L	^{241}Am μg/L	^{239}Pu μg/L
99.25	58.17	.01079	0.2786	81.77	44.05

*Raffinate values are corrected for dilution of feed by the scrub solution.

FIGURE 1. ACTINIDE DISTRIBUTION BETWEEN 30 VOL % DHDECMP IN DIPB AND HNO_3 AS A FUNCTION OF INITIAL HNO_3 CONCENTRATION.

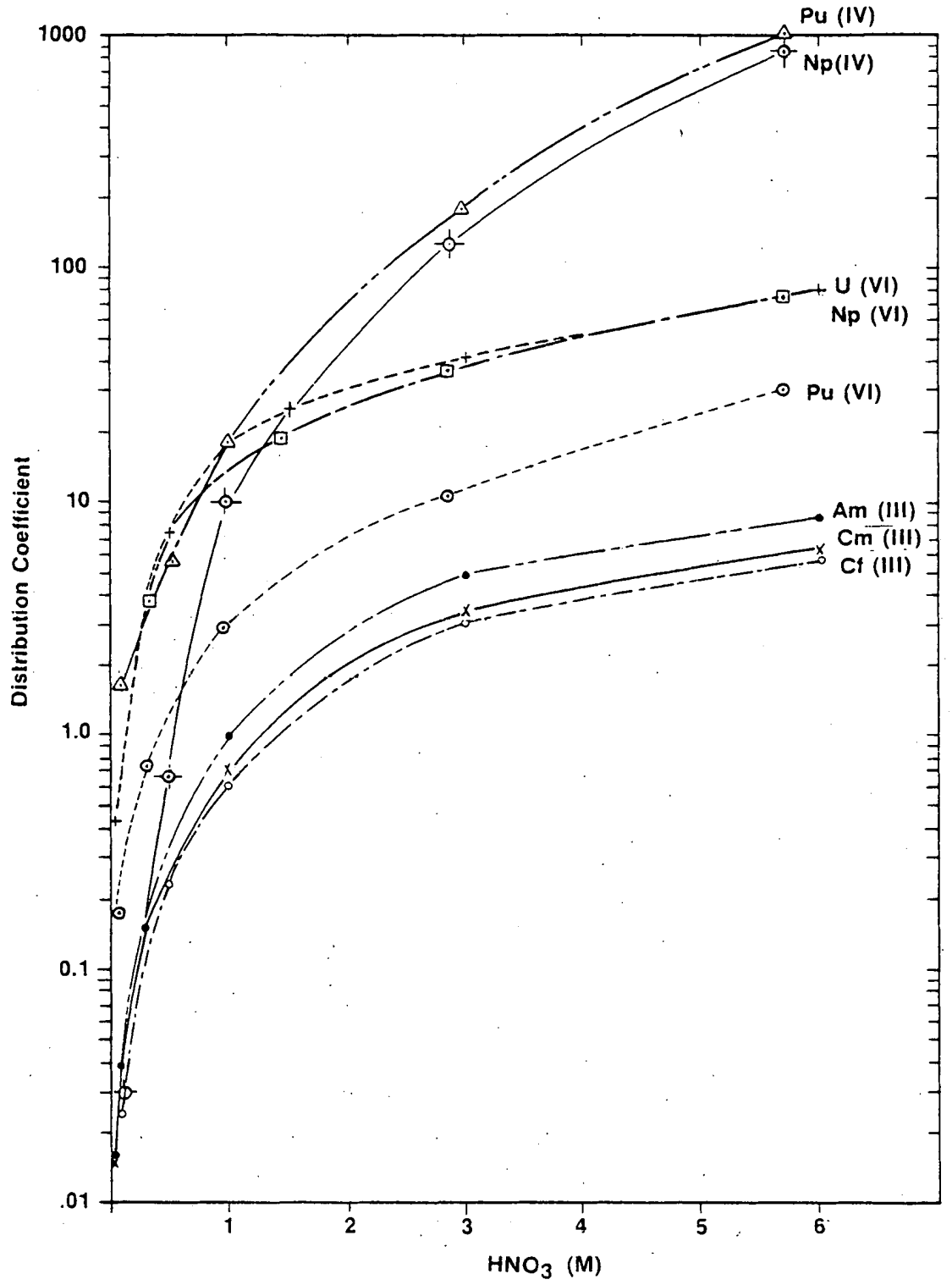

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FIGURE 2. CONCEPTUAL FLOWSHEET

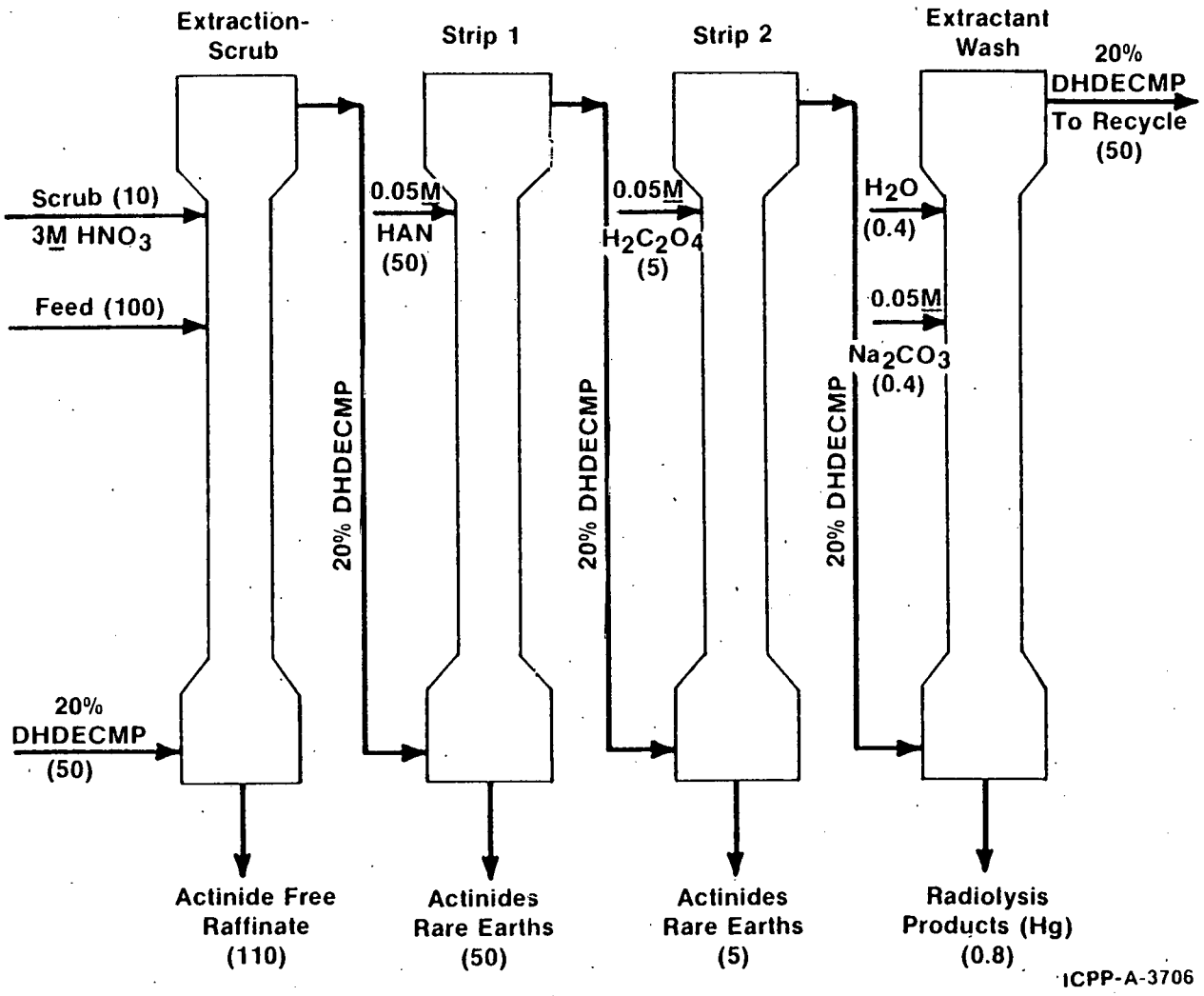
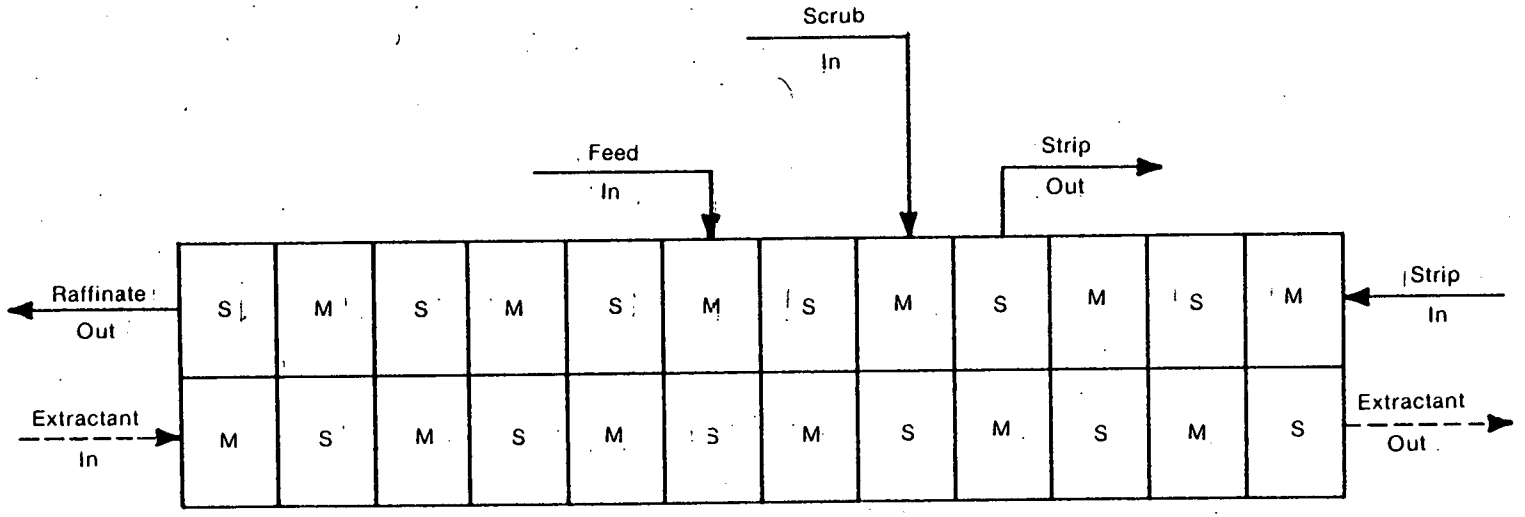


FIGURE 3. PARTIONING MIXER-SETTLER SCHEMATIC



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