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DIISOPROPYL ETHER AS A SOLVENT FOR U^{233} SEPARATION FROM THORIUM AND FISSION PRODUCTS IN CONTINUOUS COLUMN OPERATIONS

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LABORATORY SECTION

DIISOPROPYL ETHER AS A SOLVENT FOR U^{233} SEPARATION FROM THORIUM AND FISSION PRODUCTS IN CONTINUOUS COLUMN OPERATIONS

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1.0 Abstract

A continuous solvent extraction process for the recovery of Uranium-233 from thorium and fission products has been demonstrated in packed counter-current columns, using diisopropyl ether as a solvent.

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2.0 Introduction

Uranium-233 is a fissionable material which was first produced by Seaborg and Gofman in 1941[8] by the neutron bombardment of Th^{232}.

$$_{90}Th^{232}\ (n,\gamma) \longrightarrow {}_{90}Th^{233} \xrightarrow[23\ min.]{\beta} {}_{91}Pa^{233} \xrightarrow[27.4\ d]{\beta} {}_{92}U^{233}$$

Uranium-233 may be produced in gram quantities by this reaction in proposed "breeder" piles. Consequently, a feasible chemical separations process is required for the isolation of this material from bombarded thorium.

A batch solvent extraction process for 23 recovery, employing diisopropyl ether as a solvent, was successfully demonstrated on a pilot plant scale at ORNL[6,7]. Other continuous solvent extraction processes using methyl isobutyl ketone and dibutyl cellosolve as solvents were investigated by the Argonne National Laboratory[9] and by the Chemistry Division at Oak Ridge National Laboratory[1].

Based on a "cooling" period of at least eight months for the bombarded thorium, studies by the Process Design Section of the Chemical Technology Division indicated the following 23 recovery process requirements[4]:

Thorium reduction factor	10^6
Fission product decontamination	10^6
Protactinium decontamination factor	2×10^5
Overall uranium loss (%)	0.1

On the basis of these requirements and economy of operation, a continuous process was generally favored over one operated batchwise[3].

3.0 Summary

A continuous solvent extraction procedure for 23 recovery, using diisopropyl ether as a solvent, has been demonstrated in packed columns (Figure 3.0-1).

In all runs, the product solution, after one solvent extraction cycle, contained only background activity, indicating beta and gamma decontamination factors of 10^5 and 10^4, respectively. Inadequate shielding prevented the use of higher levels of activity to determine if still higher decontamination factors were obtainable. Thorium reduction factors of 10^3 were obtained through the extraction section and this separation was increased to greater than 10^4 by two scrub stages. No protactinium studies were made, but previous laboratory experiments showed a decontamination factor of 10^4 under similar conditions[6].

4.0 Experimental Results

The 1 1/2 inch diameter columns used for determining HETS values had 7.7 feet of extraction section and no scrub section, and were packed with 1/4 x 3/8 inch stainless steel split rings. The fission product decontamination studies were made in a 1 inch diameter column, having 14 feet of extraction and 10 feet of scrub section, packed with 3/16 inch Fenske packing.

The extraction, scrubbing, and stripping steps of the process were evaluated from the standpoint of 23 recovery, HETS values, thorium reduction

Experimental Results (continued)

factors, fission product decontamination, column flooding rates, and column height required to yield 99.99% 23 recovery.

4.1 Extraction Variables

Beta and gamma decontamination factors of 10^5 and 10^4 were obtained through one cycle for all runs. The lack of adequate shielding prevented the use of higher activity levels so that the effect of process variables on decontamination was not completely evaluated.

4.11 Effect of Salt Concentration

In the proposed process the salting agent for the aqueous feed would be furnished by the dissolved thorium metal from the bombarded slugs. In these particular experiments, feed solutions were made up from thorium nitrate dissolved in water, and spiked with activity from ORNL irradiated uranium slugs. The solvent was steam distilled diisopropyl ether.

The distribution coefficient ($\frac{23 \text{ org.}}{23 \text{ aq.}}$) changed rapidly with a change of $Th(NO_3)_4$ concentration, decreasing from a value of about 5 in 2.5 M $Th(NO_3)_4$ to 0.4 in 1.9 M $Th(NO_3)_4$. In the same range of salt concentration, thorium distribution coefficients (org/aq) decreased from 1×10^{-4} to 2×10^{-5} (Table 4.1-1). A similar result was observed for fission product decontamination. It was noted that $Th(NO_3)_4$ and $Al(NO_3)_3$

Effect of Salt Concentration (continued)

solutions of the same molarity gave essentially the same 23 distribution coefficient, and for solutions containing both thorium nitrate and aluminum nitrate, the salting effect was additive. This similarity of $Al(NO_3)_3$ and $Th(NO_3)_4$ salting, mole for mole, was observed for fission products as well as for 23.

Decreasing the salt concentration was observed to lower the HETS (Table 4.1-2), but the accompanying decrease in 23 distribution coefficient more than offset this apparent improvement. The net result of decreasing the total salt concentration from 2.5 M to 2.0 M was to increase the column height required for 99.99% 23 recovery from 24 feet to 89 feet. Since no appreciable increase in separation from Th and fission products was obtained by decreasing the salt concentration, 2.5 M was considered the minimum concentration.

The use of either $Al(NO_3)_3$ or $Th(NO_3)_4$ at concentrations greater than 2.5 M, even with fluoride as a complexing agent, is impractical because of the high freezing point of the solution.

4.12 Effect of Free Acid

The effect of varying free acid on 23, fission product, and thorium distribution coefficients was studied in a 2.5 molar thorium nitrate solution. This study consisted of batch equilibrations of an equal volume of an extraction feed with diisopropyl ether. All variables were held

Effect of Free Acid (continued)

constant throughout the series except the concentration of free acid in the aqueous feed which was varied by adding concentrated HNO_3 or NH_4OH.

It was found that the fission product and thorium distribution coefficients (org/aq.) increased rapidly at acid concentrations greater than 0.0 N free HNO_3. The corresponding increase in 23 distribution coefficients did not compensate for the increase in fission product extraction as shown by the separation factors in Table 4.1-3. From the result of these studies, the optimum free acid concentration for extraction was chosen as 0.0 N. This degree of acidity was accomplished in the process by neutralizing four parts of 0.1 N feed with one part of 0.4 N HNO_3 deficient scrub.

4.13 Effect of Temperature on 23 Extraction

Three factors were considered in choosing the process temperature: 23 distribution coefficients, separation from fission products, and column operability. The change of fission product decontamination with temperature was shown to be very small[7]. The 23 distribution coefficients varied from about 20 at 0°C to 1 at 50°C. Since 5 is an acceptable 23 distribution coefficient, and since there is an increased tendency for the two phases to emulsify at lower temperatures, the optimum process temperature was chosen as 20 ± 2°C.

4.14 Effect of Flowrate on HETS and Thorium Reduction

A study of the effect of flowrate on HETS and thorium reduction was made with the diisopropyl ether system. These tests were carried out using equal flows of solvent and extraction feed, and all variables were held constant except the flow through the column.

The HETS for this system was markedly affected by flowrate (Figure 4.1-5). The HETS increased from 4.5 ft. at 5% of flooding (31 gal/hr/ft^2 total throughput) to 5.7 ft. at 40% of flooding (260 gal/hr/ft^2). At rates over 40% flooding the HETS increased rapidly. The reason for this is unknown.

Thorium reduction factors did not change with variations in flowrate and no large effect on 23-Th separation is to be expected by varying the flowrate.

4.15 Column Operation and Crud Formation

Although a lower HETS was obtained using 3/16 inch Fenske packing than with 1/4 x 3/8 inch Raschig rings, an insoluble gelatinous material collected in the Fenske packing and plugged the extraction column in a relatively short period of operation. This operational difficulty was studied from two different viewpoints: the prevention of crud formation, and the substitution of 1/4 x 3/8 inch Raschig rings which may be washed free of crud.

Microscopic and spectrographic analysis showed that the crud taken from

Column Operation and Crud Formation (continued)

the extraction column was similar to an insoluble material found in C.P. $Al(NO_3)_3$. Thus, it appeared that filtration of the aqueous and scrub feeds would reduce crud formation in the column. This was found to be true, but filtration with an Alsop filter using Hyflo Super-cel as filter aid did not completely eliminate crud, and column operation using Fenske packing was seriously affected after 90 hours operation using filtered feeds. In batch work it was observed that diisopropyl ether which was previously contacted with a concentrated salt solution did not form crud as readily as raw ether when contacted with the extraction feed. This was confirmed by column studies of crud formation. In one run the diisopropyl ether was contacted with 2.5 M aluminum nitrate before entering the column, and both the aqueous feed and scrub were filtered and contacted with diisopropyl ether before entering the column. Although crud formed in the prescrubbers, it was still not entirely eliminated from the extraction column.

Since cruds were not completely eliminated, it is recommended that 1/4 x 3/8 inch Raschig ring packing be used. With this packing, the 25 Pilot Plant has operated without difficulties due to crud[2]. In addition it is recommended that the aqueous feed and scrub be filtered and the solvent be pre-equilibrated with scrub solution in a packed column before entering the extraction section.

4.2 Scrubbing

The scrubbing conditions proposed for this system were chosen from data obtained in batch studies[7] and consisted of a one-fifth volume of 2.5 M $Al(NO_3)_3$, 0.4 N HNO_3 deficient. This scrub solution was contacted with the organic extract in a scrub section of about two stages. No development of the scrubbing step for this process was carried out in column work beyond determining that two scrub stages increased the fission product decontamination by a factor of 15, and the thorium reduction factor by 10^3. The calculated reflux of 23 was 5 percent.

4.3 Stripping

The strip step consisted of contacting the scrubbed diisopropyl ether carrying the 23 with demineralized water in a packed column. The 23 distribution coefficient (a/o) in stripping was ≥ 100. Less than 0.01% of the 23 was lost when one and one-quarter volumes of demineralized water and five volumes of diisopropyl ether were contacted in eleven feet of column packed with 3/16 inch Fenske packing. Essentially no separation from fission products (decontamination factor of <2) was achieved in this strip. The loss of 0.01% was acceptably low, and no crud or operational difficulties were encountered.

5.0 Conclusions

The diisopropyl ether continuous extraction process for 23 recovery was

Conclusions (continued)

developed in 1" and 1-1/2" diameter packed columns. All results obtained have been promising. Gross beta fission product decontamination factors of 10^3 were consistently obtained, and thorium reduction factors of greater than 10^6 were demonstrated. The low solvent flash point (-15°C), the required extraction column length (33 feet) to obtain 0.01% 23 loss, and the lack of flexibility are the primary objections to this solvent system. The excellent 23 separation offered by this solvent warrants further investigation at higher levels of activity.

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FIGURE 3.0-1

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SCHEMATIC DIAGRAM OF "23" SOLVENT EXTRACTION

FLOWSHEET AND EQUIPMENT

Basis: 50 kg of bombarded thorium metal containing about 75 grams of "23".

Solvent: Diisopropyl ether.

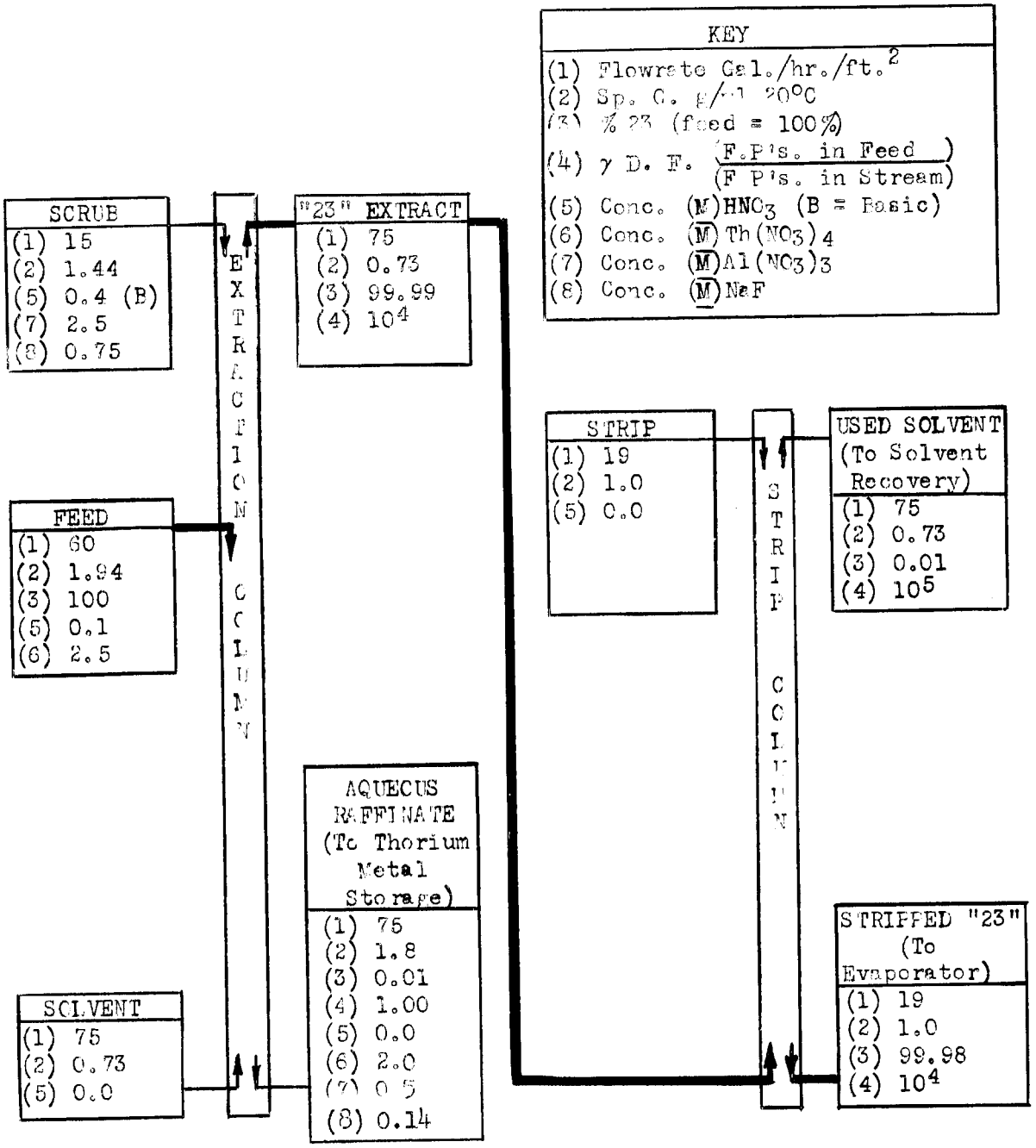

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Table 4.1-1

Effect of $Th(NO_3)_4$ Concentration on 23 and Thorium Distribution Coefficients

Extraction Feed (one volume):

$Th(NO_3)_4$ as indicated
0.01 M HNO_3
23 Tracer

Solvent (one volume):

Shell diisopropyl ether steam distilled from a caustic heel.

Temperature: 20°C ± 1°C

$Th(NO_3)_4$ Molarity	Distribution Coefficients (org/aq)	
	23	Thorium
2.5	5.0	1×10^{-4}
2.3	2.6	5×10^{-5}
2.1	1.2	3×10^{-5}
1.9	0.4	2×10^{-5}

Table 4.1-2

Effect of $Th(NO_3)_4$ Concentration on HETS and Column Height

Extraction Feed (one volume):

$Th(NO_3)_4$ as indicated
0.5 M $Al(NO_3)_3$
6 Mg/ml NaF
23 Tracer

Solvent (one volume):

Shell diisopropyl ether steam distilled from a caustic heel

Temperature: 20°C

Column: 8' x 1" pyrex glass pipe
7.5' of 3/16" S.S. Fenske packing

$Th(NO_3)_4$ M in Feed	23 Dist. Coefficient (org/aq)	HETS (Ft.)	23 Loss (%)	Calculated Column Height for 99.99% 23 Recovery (ft.)
2.0	2.8	3.5	3.5	25
2.0	3.8	3.4	3.8	24
1.5	1.2	2.2	19.	89
1.0	0.6	-	80.	-

Table 4.1-3

Effect of Free HNO_3 on 23 and Fission Product

Distribution Coefficients

Extraction Feed (one volume):

2.5 M $Th(NO_3)_4$;
HNO_3 concentration adjusted with NH_4OH or HNO_3;
23 tracer or bombarded U slug solution as spike

Solvent (one volume):

Steam distilled, Shell diisopropyl ether

Temperature: 20°C ± 1°C

HNO_3 Conc. (M)	pH	Distribution Coefficients (org/aq)		Separation Factor 23 Dist. Coeff. / F.P. Dist. Coeff.
		23	Gross Beta	
-0.8 (Basic)	0.55	2	1×10^{-5}	2×10^{5}
-0.3 (Basic)	0.25	3	1×10^{-5}	3×10^{5}
0.0	0.0	4	1×10^{-5}	4×10^{5}
0.2	<0	6	1×10^{-4}	6×10^{4}
0.4	<0	11	1×10^{-3}	1×10^{3}
0.7	<0	11	-	-
0.9	<0	11	3×10^{-3}	3×10^{3}

[redacted]

Table 4.1-4

Effect of Temperature on 23 Distribution Coefficients

Extraction Feed (one volume):

2.0 M $Th(NO_3)_4$
0.5 M $Al(NO_3)_3$
0.0 M HNO_3
23 Tracer

Solvent (one volume):

Diisopropyl ether, steam distilled from a caustic heel.

Temperature (oC)	23 Dist. Coeff. (org/aq)
0	19
10	11
15	9
20	6.0
25	4.0
30	3.5
40	1.7
50	1.3

Table 4.1-5

Effect of Flowrate On HETS And Thorium Reduction

Extraction Feed (one volume): 2.0 M $Th(NO_3)_4$
0.5 M $Al(NO_3)_3$
0.15 M NaF
0.0 M HNO_3

Solvent (one volume): Shell diisopropyl ether steam distilled from a caustic heel.

Temperature: 20°C

Column: 1-1/2" x 8' pyrex glass pipe
7.7' of 1/4" x 3/8" SS Raschig Rings

Flooding rate with equal flowrates of solvent and aqueous feed equal to 675 gal/hr/ft^2 total through-put.

Flowrate Gals/hr/ft^2 per stream	Flooding (%)	"23" DC (org/aq)	HETS (Ft)	Column Height to give 99.99% 23 Recovery (Ft.)	Thorium Reduction Factor
15.6	4.6	4.5	4.5	27	2.3×10^3
62.	18.5	4.5	5.8	35	2.4×10^3
82.	24.6	4.5	5.8	35	1.1×10^3
129.	38.	4.5	5.7	34	2.6×10^3
194.	57.	4.5	7.2	43	2.3×10^3
258.	76.	4.5	8.2	49	2.7×10^3