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Report Number: ORNL-374

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COMPARISON OF U^{233} CONTINUOUS SOLVENT EXTRACTION PROCESSES

D. E. Ferguson, R. E. Leuze

Work by:
J. L. Bamberg, G. C. Blalock,
C. V. Ellison, D. E. Ferguson
R. E. Leuze, R. C. Lovelace,
H. F. Soard, T. C. Runion

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CLASSIFICATION CHANGED TO:

BY AUTHORITY OF: TID-1148

BY: G. Manson 7/10/57

DATE ISSUED
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1.0 Abstract

This report presents a comparison of four continuous solvent extraction processes for the recovery of U-233 from thorium and fission products, using methyl isobutyl ketone, diisopropyl ether and dibutyl cellosolve as solvents.

2.0 Introduction

Uranium-233 is a fissionable material which is produced by the neutron bombardment of Th^{232} as follows:

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

Uranium-233 would be produced in gram quantities by this reaction in proposed breeder piles, and in the contemplated Materials Testing Reactor. Consequently, a feasible chemical separation process is required for the isolation of this material from bombarded thorium and fission products.

Solvent extraction processes for 23 recovery and decontamination employing diisopropyl ether were demonstrated by the Chemical Technology Division at ORNL[5,6,7]. Other 23 solvent processes using continuous extraction with methyl isobutyl ketone and dibutyl cellosolve were developed at the Argonne National Laboratory[8] and by the Chemistry Division at ORNL[1].

To enable the selection of an optimum process, four different solvent systems were evaluated in continuous countercurrent columns, involving diisopropyl ether, methyl isobutyl ketone and dibutyl cellsolve[3,4,]. This

Introduction (continued)

report represents a compiled summary of these data, with appropriate recommendations.

3.0 Summary

Four single cycle processes involving diisopropyl ether, methyl isobutyl ketone, and dibutyl cellosolve as solvents were investigated in countercurrent packed columns. All four processes yielded adequate separation of uranium from thorium and fission products. Uranium losses were satisfactory for the diisopropyl ether and methyl isobutyl ketone systems but were excessively high in stripping from dibutyl cellosolve. The results are summarized as follows:

Process	Length of Extraction Section Required for 99.99% Uranium Recovery (ft.)	Gross Beta Decontamination Factor	Gross Gamma Decontamination Factor	Thorium Reduction Factor
Methyl isobutyl ketone	17	9×10^3	$>10^3$	9×10
Diisopropyl ether	33	7×10^4	$>10^4$	2×10^3
Dibutyl cellosolve (high acid)	25	8×10^4	$>10^4$	1×10^2
Dibutyl cellosolve (low acid)	25	2×10^5	$>10^4$	4×10^2

In every case the gross gamma activity in the product solutions was at background and it was not possible to determine which solvent yielded the greatest

Summary (continued)

decontamination. Two scrub stages were sufficient to increase the thorium reduction factor to 10^4 for all of the processes. No protoactinium 233 was present, although previous laboratory results showed that a protoactinium 233 decontamination factor of 10^4 can be expected[6]. First cycle decontamination was sufficient to allow further processing of the 23 without heavy shielding.

It was concluded that both the diisopropyl ether and methyl isobutyl ketone processes yielded adequate 23 separation and recovery. However, additional studies are necessary on stripping dibutyl cellosolve before either of the two proposed processes utilizing this solvent can be used.

4.0 Experimental and Results

4.1 HETS, Column Height, Decontamination, and Thorium Reduction

The extraction, scrubbing and stripping steps of each process were evaluated from the standpoint of HETS values, thorium reduction factors, fission product decontamination, column flooding rates, and column height required to obtain 99.99% uranium recovery. The 1 1/2 inch diameter columns used for determining HETS values had 7.7 feet of extraction 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. Feed solutions were prepared by dissolving $Th(NO_3)_4$ in water,

HETS, Column Height, Decontamination, and Thorium Reduction (continued) adding 23 tracer and spiking with activity from an irradiated ORNL uranium slug. The physical properties of the solvents are listed in Table 4.1-1.

The data obtained in the extraction section (Table 4.1-2) indicated that all four processes were feasible. Although the fission product activity level was not sufficiently high to permit an accurate comparison, adequate decontamination was demonstrated with all processes.

Data obtained for the methyl isobutyl ketone system indicated that six scrub stages were sufficient to produce thorium and fission product decontamination factors of 10^5 for a one-cycle operation[4]. No decontamination studies were made for the scrub sections of the other systems.

No difficulty was encountered in stripping uranium from methyl isobutyl ketone or diisopropyl ether and losses in this step were less than 0.01%. However, in attempting to strip dibutyl cellosolve, emulsions were encountered and uranium losses were as high as 10%. Additional laboratory work is necessary to develop a satisfactory stripping operation before further consideration is given to a process involving this solvent.

4.2 Column Operation and Crud Formation

Although a lower HETS value was obtained using 3/16 inch Fenske packing instead of 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. Column plugging occurred with

Column Operation and Crud Formation (continued)

both diisopropyl ether and dibutyl cellosolve. A similar crud formed when methyl isobutyl ketone was used, but experiments with this solvent were not of sufficient length to plug the column.

Since cruds were not eliminated entirely it is recommended that 1/4 x 3/8 inch Raschig rings, which can be washed free of crud, be used. 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.

5.0 Discussion and Recommendations

From the results of these preliminary studies, a number of points were established:

(1) The diisopropyl ether process yields a very high degree of separation of 23 from thorium and fission products. On the other hand, the lack of flexibility, the low flash point of the solvent (-15°C), and the length of extraction column required for 99.99% 23 recovery (33 ft.) are strong disadvantages to this solvent system.

(2) The methyl isobutyl ketone system has none of the disadvantages of the diisopropyl ether system and offers comparable separation from thorium and fission products.

(3) It is recommended that larger scale development be confined to the study of the methyl isobutyl ketone and diisopropyl ether systems.

Discussion and Recommendations (continued)

Since additional laboratory work is necessary to develop a satisfactory method of stripping uranium from dibutyl cellosolve, and since this solvent offers no apparent advantage otherwise, it is recommended that further work on dibutyl cellosolve be discontinued.

Rex E. Leuze
Rex E. Leuze

D E Ferguson
D. E. Ferguson

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Table 4.1-1

Physical Properties Of Dibutyl Cellosolve, Diisopropyl Ether and Methyl Isobutyl Ketone

Solvent	Mol. Wt.	Sp.Gr. 20°/20°	Boiling Point °C	Flash Point °C	Solubility % by Wt.		Viscosity at 25°C Centipoises
					in H_2O	H_2O in	
Methyl Isobutyl Ketone	100	0.801	116	31.6	1.7	1.9	0.646
Dibutyl Cellosolve	102	0.838	203	85	0.20	0.6	1.45
Diisopropyl Ether	174	0.724	68.5	-9.4	0.90	0.57	0.365

Table 4.1-2

Comparison Of Extraction Data For Proposed 23 Processes

Solvent extraction carried out under simulated flowsheet conditions. (See Table 4.1-3 for more complete data on run and column conditions used in these tests).

Process	23 Dist. Coeff. (org/aq)	HETS at 20% Flooding (Ft.)	Calc. Height of Ext. Sect. for 99.99% Uranium Recovery (Ft.)	Decontamination Factor*		Thorium Reduction Factor (No Scrub Section)
				Beta	Gamma	
Methyl Isobutyl Ketone	4.0	2.5	17	$9x10^3$	10^3	9x10
Diisopropyl Ether	2.0	5.5	33	$7x10^4$	10^4	$2x10^3$
Dibutyl Cellosolve (High Acid in Feed)	5.7	5.7	25	$8x10^4$	10^4	$1x10^2$
Dibutyl Cellosolve (Low Acid in Feed)	4.4	4.1	25	$2x10^5$	10^4	$4x10^2$

* In all cases the gamma activity in the stripped product was background. Gamma activity in the aqueous feed for the methyl isobutyl ketone process was lower by a factor of 10 than for the other runs.

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Table 4.1-3

Comparison Of Solvent Extraction Data For Proposed 23 Chemical Processes

Column Size: 1 1/2" Pyrex Glass Pipe - Packing - 1/4" x 3/8" S.S. Raschig Rings.
Decontamination Runs made in 24' Column - 14' extraction, 10' scrub.
Flooding H.E.T.S. and Thorium Reduction Runs made in 7.7' column - No scrub section.

Process	Flooding Rate (gal/hr/ft^2)	Process Time For 50 kg of Thorium at 20% Flooding (Hrs.)	H.E.T.S. at 20% Flooding	23 D.C. (O/A)	Height of Extraction Section for 0.01% Loss at 20% Flooding (Ft.)	Decontamination Factors		
						Thorium* Reduction Factor (No scrub)	Gross β	Gross γ**
Methyl Isobutyl Ketone	1080	40	2.5	4.0	17	9x10	$9x10^3$	$>10^3$
Diisopropyl Ether	675	35	5.5	4.0	33	$2x10^3$	$7x10^4$	$>10^4$
Dibutyl Cellosolve High Acid in Feed	600	125	5.7	5.7	25	$1x10^2$	$8x10^4$	$>10^4$
Dibutyl Cellosolve Low Acid in Feed	900	35	4.1	4.4	25	$4x10^2$	$2x10^5$	$>10^4$

* Ten feet of Scrub Section were found to raise the Thorium Reduction Factor to more than 10^4 for all four of these systems.

** In all cases the Gamma Activity in the stripped product was background.

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Table 4.1-3 (continued)

Process Conditions

Process Description	Aqueous Feed		Scrub Solution				Flow Ratio				Temperature °C
	$Th(NO_3)_4$ M	HNO_3 M	$Al(NO_3)_3$	$Ca(NO_3)_2$	HNO_3	pH	Solvent	Feed	Scrub	Strip	
Methyl Isobutyl Ketone	1.3	0.05N Basic	1.3	None	.05N Basic	-	5	4	1	1.25	20
Diisopropyl Ether	2.5	0.1	2.5	None	0.4 Basic	-	5	4	1	1.25	25
Dibutyl Cellosolve High Acid in Feed	1.25	1.0	2.0	1.0	-	1.5*	4	2	2	1	20
Dibutyl Cellosolve Low Acid in Feed	2.0	0.2	2.4	None	-	1.8**	4	3	1	1	25

* pH adjusted with $Ca(OH)_2$.
** pH adjusted with concentrated NH_4OH.

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