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TO: F. L. Culler

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SUMMARY

CLASSIFICATION CANCELLED

DATE MAR 12 1957 *het*

For The Atomic Energy Commission

H. F. Caneel
Chief, Declassification Branch

Homogeneous Reactor Blanket Studies

A greater densification of ThO_2 was obtained by adding 1 wt % calcium than was attained previously with 1 mole %. A marked increase in sedimentation rate was observed upon adding 500 and 1000 ppm of sulfate to a ThO_2 slurry.

Homogeneous Reactor Blanket Processing

Plutonium was not coprecipitated when iron hydrolyzed and precipitated from 1.4 m UO_2SO_4 heated at 250°C under stoichiometric hydrogen and oxygen overpressure.

Americium Recovery

Americium and plutonium may be recovered from waste solutions of the plutonium isotopes separation program at Y-12 by extracting as thiocyanates the major impurities (Fe, Cu, Ni) into amyl ether, followed by anion exchange for concentrating and separating plutonium and americium.

Mass-233 Studies

Thorium and uranium may be stripped together using 0.008 M HNO_3 in a column containing nine stages. The optimum A/O flow ratio lies between 1 and 2. Ten additional scrub stages gave only slight increase in decontamination in Thorex A-column tests.

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Homogeneous Reactor Chemical Processing

The efficacy of metal surfaces in suppressing the effect of ruthenium on iodine chemistry at elevated temperatures is slight. Conversion of metal oxides to sulfates at room temperature after an initiation period at 165-170°C has been observed.

Thorex Second Uranium Cycle

About 2.2 kg of U²³³ was processed through a second uranium cycle during the week of June 11-15. The product met shipping specifications.

Excer

A product concentration of 177 g U/l and a recovery of > 99.8% was obtained from synthetic ore leach with the 2-in. contactor.

Feed Materials

Hermex. The dissolution rates of uranium in 0.1 wt. % Mg amalgam was about twice that in mercury alone, resulting in a nearly saturated solution, 1.5 wt. % in U.

Metallex. In studies of factors affecting the free voidage in sintered thorium metal, increasing cold-pressing pressures decreased free voidage, while pressing under inert atmosphere rather than air appeared to have no effect. Use of tail-end washing procedures, such as methanol rinsing and methanol rinsing followed by vacuum drying appeared to have no effect on voidage. Substitution of anhydrous methanol for water in amalgam washing increased problems in amalgam filtration and unwanted extrusion from the die when cold pressing.

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3.0 AMERICIUM RECOVERY (R. E. Leuze and R. D. Baybarz)

3.1 Tentative Process

1. Feed preparation:

- a. Neutralize waste solution to a pH of 2-3 with NaOH.
- b. Add sufficient NH_4CNS to complex all ions and give about 0.3 M excess.

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2. Extraction and scrubbing:

a. Batch extract with 2 or 3 equal volumes of amyl ether to remove copper, iron, and nickel thiocyanates.

b. Scrub ether with 2 one-half volumes of water to remove any extracted plutonium or americium.

3. Concentration by anion exchange:

a. Combine aqueous phases from extraction and scrubbing and make $4.0 \text{ M } \text{NH}_4\text{CNS}$.

b. Pass solution through Dowex-1 anion exchange resin to sorb both americium and plutonium.

c. Elute americium and plutonium with $0.25 \text{ M } \text{NH}_4\text{CNS}$ (about 90% removal in 3 column volumes and 99% in 6-7 column volumes).

4. Pu and Am separation by anion exchange:

a. Make eluate from first anion resin column $8 \text{ M } \text{HCl}$.

b. Pass solution through a second Dowex-1 anion exchange resin column to sorb plutonium.

c. Elute plutonium with $0.1 \text{ M } \text{HCl}$ in ~ 2 column volumes.

Due to the inner orbital (covalent) complexing of Fe with the thiocyanate forming $\text{Fe}(\text{CNS})_3^{-3}$ an irreversible extraction of the $\text{Fe}(\text{CNS})_3^{-3}$ is achieved with organic ethers. Both copper and nickel behave in a similar way. Amyl ether was chosen as the organic extractant due to its physical properties, such as high flash point ($\sim 134^\circ\text{F}$), high boiling point (190°C), and extremely low solubility in water.

The extraction of Fe, Cu, and Ni is carried out at oxidizing acid concentrations of $< 0.5 \text{ M}$. This is to prevent oxidation of the thiocyanate ion to thiocyanogen, $(\text{CNS})_2$, thereby decreasing the free $(\text{CNS})^-$ content and preventing complete complexing and extraction of the impurities. The Pu and Am present in the waste solution form ionic or outer orbital complexes of the order $\text{Pu}(\text{CNS})_x^{4-x}$ and $\text{Am}(\text{CNS})_x^{3-x}$. The

number of $(\text{CNS})^-$ ions present in the Am and Pu complex is unknown but it is presumed that the complexes are ionic rather than covalent since they do not extract in organic ethers. Complexing of Am is quite strong with thiocyanate and is stable at a pH of 4 or less.

3.2 Alternate Ion Exchange Methods

After the impurities have been extracted with amyl ether, the aqueous phases from extraction and scrubbing may be combined and passed through Dowex-50 cation exchange resin to sorb both the americium and plutonium at $<0.5 \text{ M } \text{NH}_4\text{CNS}$ concentration. Elution with about 20 column volumes of $0.25 \text{ M } \text{H}_2\text{SO}_4$ will remove 90% of the plutonium. Elution with about 3 column volumes of ammonium acetate-citric acid will remove the remainder of the plutonium and the americium.

The americium and plutonium may be eluted from the cation resin with about 10 column volumes of $10.8 \text{ M } \text{HCl}$. The plutonium may then be loaded on a Dowex-1 anion column to separate it from americium.

4.0 MASS-233 STUDIES (R. H. Rainey)

4.1 Thorex AC-ABC Two-Cycle System (A. B. Meservey)

The optimum flow ratio of aqueous $0.008 \text{ M } \text{HNO}_3$ to the organic AU stream for stripping thorium and uranium together in 9 stages was found to lie between 1:1 and 2:1. The 1:1 flow ratio required 30 volume changes to reach equilibrium due to the low concentration of uranium in the feed and the high concentration required to cause uranium to break through against the thorium salting in the lower section of the strip column.

4.2 Effect of Additional Scrub Stages on Decontamination in Thorex A-Column (A. B. Meservey)

Ten additional scrub stages in the Thorex A-column gave only slightly greater fission product and protactinium decontamination than the original eight scrub stages, and would not appear to be an effective substitute for mechanical filters on a second solvent extraction cycle. The test was made in countercurrent batch extractions using cold feed spiked with hot feed to give 2×10^7 c/m/ml in both β and γ activities.

5.0 HOMOGENEOUS REACTOR CHEMICAL PROCESSING (R. A. McNees)

5.1 Iodine Chemistry (S. Peterson)

Equipment modifications necessary for studying the effect of gamma radiation on iodine behavior at elevated temperatures have been completed. Experimental work is expected to start next week.

Further tests of the efficacy of metal surfaces in overcoming the effect of ruthenium on the behavior of iodine have shown the effects to be less pronounced than previously thought.

5.2 Solids Dissolution (R. A. McNees)

Complete dissolution (less than 0.1% residue) of simulated reactor solids was obtained by treating 5 g of solids with 50 ml of 10.8 M sulfuric acid for four hours at 165-170°C followed by digestion at room temperature for 65 hours. Addition of an equal volume of water gave a solution which has been stable for several days. It is interesting to note that conversion of the brown oxides to white sulfate salts

was apparently about 50% complete at the end of the four hour heating period but continued to completion during the time they were at room temperature. The synthetic solids contained iron, zirconium, chromium, copper, and rare earths and had been prepared by heating hydroxide of these elements at 285°C in 0.02 m UO_2SO_4 , 0.005 m H_2SO_4 for 16 hours and then drying at 105°C before use.

6.0 THOREX SECOND URANIUM CYCLE (J. R. Flanary, J. H. Goode)

The remainder, about 2.2 kg, of the 4.2 kg of off-specification U^{233} returned to ORNL for reprocessing was processed in the 0.75-in. diameter pulse columns during the week of June 11-15. Excessive feed acidity (i.e., 1 M excess HNO_3 rather than 0.5 M) caused abnormal extraction losses during one run; under these conditions the aqueous raffinate contained about 0.2% of the uranium. Normal losses to the AW, using a 0.5 M HNO_3 feed, are about 0.001%. A material balance of 100% was obtained for the 4 kg processed. Product bottles continued to meet specifications for fission product activity.

7.0 EXCER (I. R. Higgins)

Runs are continuing with the 2-in. contactor using synthetic ore leach feeds and 8 M HCl -water elution to prepare UO_2Cl_2 for electrolysis. The feed also contains the UO_2F_2 recycle supernate from the previous electrolysis. On the 3 ft. loading section of

Permutit SK, 20-40 mesh, and a loading of 40 g U/l, the recovery was greater than 99.8%. About 3 lbs of HCl was consumed per pound of U to strip the sulfate in 3 ft of column section. Product concentrations are becoming progressively higher as the runs continue. A maximum draw-off of 177 g U/l and a 225 g U/l sample was obtained just below the product take-off point. The system appears very satisfactory, but to date the column sections have been cramped for lack of height. As soon as a place can be found to install longer column sections, maximum production rate, minimum loss, minimum HCl consumption, and maximum product concentration will be demonstrated.

8.0 FEED MATERIALS (O. C. Dean)

8.1 Hermex (E. Sturch)

8.1.1 Dissolution of U in Boiling Mg Amalgam

The dissolution rate of U in boiling 0.1 weight % Mg-amalgam was shown to be about twice as great as in mercury alone. About 1.4 g of U was dissolved in 135 g of Mg-amalgam during the initial 5 minutes using a uranium wafer having a surface area of 15.4 cm². The rate dropped rapidly with time and only 2 g were dissolved in the first hour, giving a nearly-saturated solution of about 1.5 weight % U in Mg amalgam.

8.2 Metallex

Studies of the effects of varying washing techniques and cold-pressing pressures on the percentage of atmosphere-connected voidage in the sintered thorium metal were continued. In a series of

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A thorium amalgam, reduced at 130°C for 1/2 hr was washed with HCl sparged-anhydrous methanol to remove excess Na, NaCl, and unreduced thorium compounds. This was followed by rinsing with argon-sparged methanol to remove residual HCl. Attempts at cold-pressing the washed product resulted in extrusion of the compacted amalgam from the die. Use of felt pads on the lower die plug and the upper ram prevented extrusion, but the product pellet was extremely reactive to air.

PC Blance

R. E. Blanco

O E Ferguson

D. E. Ferguson

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