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D. E. Ferguson

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SUMMARY

Homogeneous Reactor Fuel and Blanket Studies

In LITR slurry irradiation experiment No. 24 the stirring stopped after 92 hours at full reactor power. MoO_3 concentrations of 0.025 and 0.075 m gave gas recombination rates of 0.67 and 0.14 moles of H_2 per hour per liter of slurry under simulated reactor blanket conditions.

Homogeneous Reactor Blanket Processing

Preconditioning titanium and Zircaloy-2 disks by the HRT procedure did not appreciably affect the amount of plutonium adsorbed from uranyl sulfate solution at 250°C.

Feed Materials

A coating of titanium was deposited on Zircaloy-2 in a fused NaCl bath by placing a specimen of Zircaloy-2 near a specimen of titanium metal in the same melt.

Heterogeneous Reactor Processing

The Zircex hydrochlorinator product is primarily UCl_3 . The particle size of desublimed ZrCl_4 is increased by increasing the desublimation temperature.

Excer

From continuous runs there are indications that UO_2Cl_2 product may be withdrawn at a concentration as high as 140 g U/l and containing only 0.05 M NaCl.

Thorex Second Uranium Cycle

Five batches of U^{233} product from the Thorex pilot plant, totalling 4000 g, have been processed through the solvent extraction equipment in Bldg. 3550. The uranium loss was 0.05% and all products have met activity specifications for shipment.

1.0 HOMOGENEOUS REACTOR FUEL AND BLANKET STUDIES (J. P. McBride)

1.1 In-Pile Irradiation (A. R. Jones, N. A. Krohn)

In LITR experiment No. 24 the bomb stirred well for 121 hr in-pile (92 at full power). The stirrer stopped operating suddenly while the reactor power was constant. It could not be restarted. As the bomb could not be removed from the liner the latter was removed from the reactor and buried.

1.2 Gas Recombination Studies (L. E. Morse)

For a mixed oxide slurry containing 0.075 molal MoO_3 , tested as prepared in the temperature range 250-290°C, experimental results for the H_2 - O_2 reaction rates were fitted by the least squares relation

$$k = 1.84 \times 10^{18} e^{-\frac{23,080}{T}}$$

where

k = specific reaction rate constant (hr^{-1})

T = absolute temperature.

At 280°C, the reaction rate was equivalent to the consumption of 0.67 moles H_2 per hour per liter of slurry at a partial pressure of 500 psi H_2 .

The reaction rates for the slurry containing 0.025 molal MoO_3 , tested as prepared in the temperature range 250-290°C, were fitted by the least squares relation

$$k = 1.73 \times 10^3 e^{-\frac{17,380}{T}}$$

At 280°C the reaction rate was equivalent to the consumption of 0.14 moles H_2 per hour per liter of slurry at a partial pressure of 500 psi H_2 .

The slurries were prepared by tumbling the dry ThO_2 , $\text{UO}_3 \cdot \text{H}_2\text{O}$ and MoO_3 for one hour and then heating in water for 3 hours at 280°C in the presence of oxygen.

2.0 HOMOGENEOUS REACTOR BLANKET PROCESSING (R. E. Leuze)

2.1 Plutonium Adsorption on Metals (J. M. Chilton)

Preconditioning titanium and Zircaloy-2 metal disks by the HRT procedure did not appreciably affect the amount of plutonium adsorbed from uranyl sulfate solution at 250°C .

Cold-rolled titanium and rolled Zircaloy-2, both polished and unpolished, were preconditioned by the procedure to be used on the HRT. This procedure is as follows: (1) clean with 3% trisodium phosphate and follow with 5% nitric acid, (2) heat 100 hr in water at 250°C under 400 psi oxygen, and (3) heat 400 hr in 1.4 M UO_2SO_4 at 250°C under 400 psi oxygen. Both conditioned and unconditioned metal disks were exposed 15 hr at 250°C to 1.4 M UO_2SO_4 containing 4 mg Pu/kg H_2O under 100 psi oxygen and 200 psi hydrogen. Plutonium adsorption on conditioned and unconditioned Zircaloy-2 (not polished) was 1.5 and $2.0 \mu\text{g}/\text{cm}^2$, respectively. Plutonium adsorption on conditioned and unconditioned Zircaloy-2 (polished) was 0.77 and $0.74 \mu\text{g}/\text{cm}^2$, respectively. The unconditioned titanium adsorbed $0.062 \mu\text{g Pu}/\text{cm}^2$, and the conditioned titanium adsorbed only $0.031 \mu\text{g}/\text{cm}^2$. However, this may not indicate a real effect since duplicate tests vary this much.

3.0 FEED MATERIALS (O. C. Dean)

3.1 Metallex

3.1.1 Coating Zircaloy-2 with Titanium (C. P. Johnston)

Experiments were carried out to determine the feasibility of using an adaptation of the method of Schlechten, Straumanis and Gill¹ for deposition of titanium on Zircaloy-2 from pyrosols. Specimens of Zircaloy-2 and titanium metal $\sim 1 \times 2 \times 0.2$ cm were separated by one-millimeter nichrome wire and held in position by wrapping the wire around the two pieces. They were then placed in small porcelain crucibles containing molten NaCl at temperatures of 900 and 940°C in separate experiments for periods of 16 hr each. After removing the crucible and contents, cooling and dissolving the salt from specimens, a dark gray deposit was found on the Zircaloy-2 on the side next to the titanium metal. The Zircaloy samples were found to have lost ~ 0.1 to 0.2 g per 3 gram sample while the titanium samples lost about 3 times this weight per sample of 1-2 g each. The loss of weight of independent Zircaloy-2 samples immersed in molten NaCl for 16 hr at corresponding temperatures were about twice that of Zircaloy samples wired to titanium.

Analysis of the coated Zircaloy specimen by microspectrographic analysis indicates fairly even distribution of titanium on the sample. Other samples have been submitted to the Metallurgy Division for metallographic examination and to the electron microscopy section of Analytical Chemistry Division for electron-microscopic examination.

Two samples of Zircaloy-2 treated with titanium quasi-amalgam in an attempt to deposit titanium on the surface failed to give a sufficient coating of titanium to be detected by metallographic or

1. J. Electrochem. Soc., 102, 81-5 (1955).

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microscopic examination although microspectrographic examination showed Ti.

4.0 HETEROGENEOUS REACTOR PROCESSING (J. E. Savolainen)

4.1 Chloride Removal from APPR Dissolver Solution (M. L. Hyman)

The continuous distillation column described in last week's report was successfully used to strip chloride from a synthetic APPR dissolver solution originally containing 70 g/l stainless steel and 16.8 g/l U and which was 2.4 N HCl.

The column feed was diluted fourfold and fed into the top of the column at D/F = 2. The stripping vapor, which was 15.2 M HNO_3 was generated in an external reboiler.

The stripped feed, collected as the column bottoms in a separate receiver, analyzed <10 ppm chloride and contained all the U in the feed. The distillate recovered 90% of the chloride in the feed.

A second run, using the same feed solution, but with a D/F = 3, again gave complete recovery of the U in the stripped bottoms. However, in this case only 81% of the chloride was recovered in the distillate.

There was no evidence of "denitration" of the $\text{UO}_2(\text{NO}_3)_2$ (as has been suggested as a possibility) even at the 115-120°C temperatures encountered in the column.

4.2 Hydrochlorination (J. E. Savolainen)

Chemical analyses indicate that uranium is present as the tri-chloride after removal of the zirconium from a uranium-zirconium alloy.

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The Cl/U ratio was found to be 3.04. X-ray diffraction patterns also show that no detectable UCl_4 is present. Evidently the presence of hydrogen gas formed during the hydrochlorination is sufficient to maintain the uranium in the trivalent state. The formation of the uranium trichloride permits higher operating temperatures in the hydrochlorinator. The physical properties of UCl_3 may permit operation at 700°C.

4.2.1 Recovery of Zirconium Tetrachloride Powder
(L. A. Lee and M. A. Welt, MIT Practice School)

The particle size of zirconium tetrachloride desublimed from the product vapor from a Zircex hydrochlorinator is increased by increasing the desublimation temperature. A simple cooler to desublimates the zirconium tetrachloride followed by two cyclones and a trap were sufficient to recover essentially all of the zirconium tetrachloride. The particle size and distribution was obtained by measuring and counting using photomicrographs of the product.

4.3 APDA Fuel Processing - Comparison of H_2SO_4 and HF Dissolution Systems (A. H. Kibbey)

The proposed APDA fuel element has a 0.150-in.-dia 10% Mo-U alloy core, clad with 0.004-in. thick Zr metal. Removal of the thin Zr cladding by dissolution in 900% excess 14 M H_2SO_4 , assuming the formation of $ZrOSO_4$, or 100% excess 10 M HF, assuming formation of ZrF_4 , followed by core dissolution in 8 M HNO_3 and subsequently adjusting this dissolver solution to 2 M HNO_3 prior to solvent extraction was considered. The amounts of the various reagents required per kg of fuel and the adjusted solvent extraction feed composition calculated for each system are summarized in Table 1.

Table 1

Cladding Dissolution System	Reagents Required/kg of Feed, liters			Solvent Extraction Feed Composition
	Cladding Dissolution	Core Dissolution (8 M HNO ₃)	Feed Adjustment (16 M HNO ₃)	
900 excess* 14 M H ₂ SO ₄	0.288	4.386	0.688	Free NO ₃ ⁻ = 2.0 M SO ₄ ⁻² = 0.75 M Zr ⁺⁴ = 0.075 M UO ₂ (NO ₃) ₂ = 0.678 M Mo = 0**
100% excess 10 M HF	0.322	4.386	0.672	Free NO ₃ ⁻ = 2.0 M F ⁻ = 0.60 M Zr ⁺⁴ = 0.075 M UO ₂ (NO ₃) ₂ = 0.67 M Mo = 0**

* Optimum condition determined at Idaho (IDO-14035).

** Precipitates quantitatively as molybdic acid.

A concentration of 0.75 M sulfate in the solvent extraction feed is high, but is permissible, since 1.0 M sulfate or less is considered tolerable. The F⁻ concentration of 0.3 M, not complexed by zirconium, is undesirable from the standpoint of corrosion. Dilution of these feeds with more nitric acid to minimize the deleterious effects of the SO₄⁼ or F⁻ would not only dilute the uranium, but would also necessitate incorporation of an expensive acid recovery step in the process in order to minimize the volumes of aqueous waste to be stored. On the basis of these calculations, Zr jacket removal by H₂SO₄ or HF dissolution appears feasible.

4.3.1 Dissolution of Uranium Metal and Si-U Alloy (A. H. Kibbey)

The boiling point dissolution rates of 2% Si-U alloy in 6 M and 14 M H₂SO₄ and in 8 M HNO₃ were determined to be 0.052, 0.11 and 22.95

mg/cm²/min, respectively. In addition, a dissolution rate of 0.258 mg/cm² was determined for uranium metal in boiling 14 M H₂SO₄. These results, together with data previously reported for 0.5 and 1% Si-U alloys are tabulated in Table 2.

Table 2

Percent Si in Alloy	Dissolution Rate, mg/cm ² /min		
	6 M H ₂ SO ₄	14 M H ₂ SO ₄	8 M HNO ₃
0	0.032	0.258	---
0.5	0.043	---	58.15*
1	0.064	---	76.74*
2	0.052	0.11	22.45

* Decreased rapidly owing to adherent SiO₂ deposit forming on the surface.

5.0 EXCER
(I. R. Higgins)

Another batch of UO₂Cl₂ has been prepared starting with a synthetic contaminated sulfate ore leach. This time the 5 M NaCl was used once, rather than recycled by adding CaCl₂. The final product composite was 0.5 M in NaCl, but this is limited by the control on rate of product removal. A 53 g U/l product was withdrawn which was 0.05 M NaCl. A peak concentration of 140.6 g U/l was obtained, indicating that this quality product may be withdrawn continuously.

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

Recently the Bldg. 3550 3/4-in.-dia pulsed-column equipment has been modified to provide a second solvent-extraction cycle for the Thorex U^{233} product from the pilot plant. Owing to pilot plant operational difficulties, the U^{233} product, which has been separated from thorium and gross fission products by one solvent-extraction cycle and concentrated by ion exchange, contains too much fission product activity to be accepted by Los Alamos. Hence, a second cycle is needed for additional decontamination.

Since the U^{233} product is eluted from the ion-exchange column with acetate-citrate solution, a special second cycle chemical flow-sheet was developed to recover and decontaminate the uranium in existing equipment. Laboratory tests showed that the addition of 4.5 M HNO_3 per liter of product was sufficient to convert the uranyl-acetate-citrate complex to TBP-extractable uranyl nitrate. Aluminum nitrate was added to provide high salting strength needed to gain quantitative uranium extraction with only 8 ft of extraction column height. A scrub of 3 M HNO_3 was chosen for scrubbing out fission products, based on previous experience with similar systems. It also serves to reduce entrainment of aluminum in the product stream.

Table 3 shows the second cycle chemical flowsheet. The flow rates are those actually employed in process, and represent a uranium mass throughput of 72 g/hr. The rates are about 85% of flooding; thus the system's capacity is 1.73 kg U/24 hr. Product is received in 800-1000 g batches and, owing to criticality considerations, is adjusted to feed batches limited to 300 g. Pulsed column operation, however, is continuous; about 14 hr are required to process 1 kg. The decontaminated product (35 g U/l and 0.2 M HNO_3) is collected in 4-liter plastic bottles and returned to the pilot plant for concentration and shipment to Los Alamos.

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Table 3

Thorex Second Uranium Cycle Chemical Flowsheet

Feed	25 ml/min	48 g U/l, 1.5 M $\text{Al}(\text{NO}_3)_3$, 0.5 M HNO_3 , 0.3 M citric acid, 2 M acetic acid 1.7 M NH_4NO_3
Scrub	6 ml/min	3 M HNO_3
Solvent	34 ml/min	15% TBP in Amsco 125-82
Strip	34 ml/min	0.01 M HNO_3

To date, 5 batches of product totalling 4083.5 g have been processed and returned to the pilot plant. Uranium lost to the aqueous and solvent waste streams totaled 2.098 g, or 0.051%. Typical decontamination factors for the operation are: gross beta $>10^4$, gross gamma 180, Ru beta 1.5×10^4 , Zr-Nb gamma 38, and TRE 13. All second cycle products have met Los Alamos activity specifications. Except for occasional feed pump freeze-up owing to supersaturated feed during the third run, the operation has been highly satisfactory.

R. E. Blanco
R. E. Blanco

D. E. Ferguson
D. E. Ferguson

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