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SUMMARY

Feed Materials

Metallex

Metallographic examination of Ti-coated Zircaloy-2 from a molten NaCl treatment indicate an alloy at grain boundaries of the coating.

As the free voidage percentage of thorium metal increases, the oxide, nitrogen and hydrogen contents of the metal and its hardness also increase. Residual water in the amalgam at the beginning of the sintering step is suspected as a cause for increased free voidage.

Hermex

The rate of dissolution of uranium in bismuth amalgam is less than in mercury or sodium amalgam. The stability of bismuth-uranium amalgam to oxygen is greater than that of uranium amalgam and comparable to that of uranium-sodium amalgam.

Homogeneous Reactor Fuel and Blanket Studies

Oxide prepared by the hydrothermal decomposition of thorium nitrate was comparable to that obtained from the oxalate by the same method. The use of an aluminum container contributed significant Al contamination to the product oxide from hydrothermal oxalate decomposition.

Uranium-233 Isolation

Poor uranium sorption in Thorex Pilot Plant Run HD-17 was not due to interfering cations or complexes. There is no apparent reason chemically why the uranium did not sorb.

Thorex Second Uranium Cycle

This week, about three-fourths of 4000 grams of contaminated Thorex first cycle uranium product which was returned to ORNL for reprocessing

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has been decontaminated by a second uranium cycle in the 3550 Bldg. facility. Losses totaled 3 grams and the product met activity specification for shipment.

Heterogeneous Reactor Fuel Reprocessing

Dissolution of PWR Fuel into H_2SO_4

Zircaloy-2 clad fuel elements containing UO_2 can be dejacketed chemically with boiling H_2SO_4 . The amount of uranium dissolved from the solid UO_2 was only 0.2%.

Hydrochlorination

Some zirconium and niobium decontamination of uranium is obtained on hydrochlorination. Ruthenium, the rare earths and strontium remain with the non-volatile UCl_3 . The cesium activity tends to divide evenly between the $ZrCl_4$ and the non-volatile UCl_3 .

Excer

A tap density of 3.1 has been obtained on a UF_4 product prepared from synthetic ore leach.

Ion Exchange Studies

The 1 inch column for rare earth separation studies has been installed. Instrument and electrical connections will delay testing for about 2 weeks.

Mass -233 Studies

Scavenging of Pa from periodic pilot plant samples of AP by precipitation with NaOH or HIO_3 continue to give over 99% removal of the Pa.

No effect was noted when versene was added to Thorex AS solution.

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1.0 FEED MATERIALS (O. C. Dean)

1.1 Metallex (O. C. Dean)

1.1.1 Metal Quality Studies

The relationship between metal quality of sintered thorium and the percentage of free voidage was further studied, and results are presented in the following table. The data show that higher oxide, higher nitrogen, and higher hydrogen contents coincide with the higher free voidage values. One exception is noted. The TAS 13-1 methanol-washed and the TAS 13-2 water-washed are inverted with regard to free voidage, oxide and hydrogen contents.

It has been observed previously that amalgams reduced at higher temperatures are more reactive, and the data in the table support this observation.

The high oxide contents of the unpickled specimens indicated in the vacuum fusion results for the TAS-13 samples shows that the increased surface exposed to atmosphere during sintering increases oxygen pick-up. The nitrogen analyses parallel the oxygen analyses, and since nitrogen is inactive with thorium at low temperatures it is assumed that the pick-up of both nitrogen and oxygen occurred during retorting. The effectiveness of pickling the more porous sinters is also seen. The theory that residual water in the amalgam is deleterious to the metal quality receives support in the data in the following table.

Upsetting samples of sinters represented in the table by pressing to 50% thickness required more pressure by a factor of 1.5 in the case of the higher voidage samples, and resulted in metal ~ 1.65 times as hard.

Work is in progress in an attempt to improve washing techniques and slug pressing of thorium quasi-amalgam under inert atmosphere. A small laboratory Carver press was installed in a vacuum dry box and several pressings completed.

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The Relationship of Metal Quality to Free Voidage^(a)

Sintered Metal No.	Final Washing Treatment	Percent Free Voidage ^(a)	ThO ₂ by HCl-ins	ThO ₂ by vacuum ^(a) fusion	Reduction Temp. °C	Hydrogen ppm	Nitrogen ppm
TAS-12-1	Vacuum-dried	7.47	0.49	0.54	130	17	21
TAS-12-2	Water-washed	13.20	1.25	1.40	130	54	26
TAS-12-3	Methanol-washed	11.70	0.87	1.40	130	48	63
TAS-13-1	Methanol-washed	37.10	0.73	3.63	200	110	390
TAS-13-2	Water-washed	34.60	0.44	4.29	200	150	450
TAS-13-3	Vacuum-dried	29.00	0.42	2.56	200	74	270

(a) Free voidage indicates the voids exposed to atmosphere.

(b) Sintered metal was not pickled prior to the oxygen determination as it was in the case of acid insoluble ThO₂

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

Exploratory runs are under way to determine the feasibility of adopting the method of R. Shorski for depositing titanium on steel to depositing titanium on Zircaloy-2. The procedure consists of heating the test specimen in a molten mixture of NaOH and TiO_2 at $890-920^\circ C$ for periods of 4 hr or longer, in graphite containers.

Metallographic and electron-microscopic examinations of titanium deposited on Zircaloy-2 from molten NaCl and metallic titanium are incomplete. However, metallographic examination indicates an alloy type formation at the grain boundary of the deposit.

1.3 Hermex (E. Sturch)

1.3.1 Dissolution of U in Boiling Bi-amalgam

Dissolution studies showed that the rate of U dissolution in Bi-amalgam is less than that in mercury or Na amalgam.

The rate of dissolution of a disk of U in Bi-amalgam was about $1/4$ that in mercury and slightly less than the dissolution rate in Na-amalgam. The saturation solubility was not reached after 5 hours of dissolution and is in excess of 0.6% U.

The stability of the U-Bi-amalgam was found to be greater than that of the U-amalgam and comparable to the stability of the U-Na-amalgam. There appeared to be an oxide-film formed at the amalgam-air interface in the case of the U-Bi-amalgam.

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

2.1 Alternate Methods of Oxide Preparation (V. D. Allred, C. E. Schilling)

Oxides apparently comparable in quality to that obtained from oxalate has been prepared by the hydrothermal decomposition of 0.9 M thorium nitrate solutions. The resulting oxide has a crystallite size of the $130 \text{ \AA}$ which

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is one half of that for oxide from hydrothermally decomposed oxalate. There was little indication of crystallite growth with firing at temperatures up to 900°C. Nitric acid recovery from the process was about 95% of theoretical quantity.

Oxide prepared from hydrothermally decomposed thorium oxalate in an aluminum container showed an increase in the aluminum to thorium ratio from 280 ppm to 850 ppm. Aluminum contamination of a coprecipitated thorium-uranium oxide, 0.37 mole % U, increased from 56 to 120 ppm.

3.0 URANIUM-233 ISOLATION (W. E. Tomlin)

During Thorex Pilot Plant Run HD-17, most of the uranium did not sorb on the Dowex-50 resin column. In a small scale test using a sample of this solution, uranium sorption on new Dowex-50 resin was normal. Furthermore, reconditioned resin from the Pilot Plant had a normal uranium capacity of about 250 g/l. Therefore, the poor uranium loading does not appear to be caused by interfering cations or complexes.

A sample of the uranium solution that failed to sorb on the Pilot Plant resin column had a pH of 1.45 and contained 0.15 mg U/ml and small amounts of Na, Th, Fe, Cr, Si, and Ca. When 650 ml of this solution was passed through 50 ml of new Dowex-50 resin, the uranium loss in the effluent was less than 0.3%.

When 50 ml of reconditioned resin from the Pilot Plant column was loaded to break-through with a normal uranium solution, 12.34 grams of uranium was sorbed. This is 247 g U/liter or about 90% of the theoretical capacity.

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

About 4150 g of Thorex first cycle U-233 product, previously shipped failed to meet activity specifications and was returned to ORNL. Currently, this material is being processed in the second uranium cycle (Bldg. 3550) in

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a series of five runs. To date, 2920 g have been processed and transferred to the pilot plant for concentration and shipment. For the first two runs, uranium lost to the aqueous and solvent waste streams totalled 3 g. Cutie pie readings taken on 150 g batches of the U-233 second cycle product were about 50 mr at contact, consistent with product from previous runs.

5.0 HETEROGENEOUS REACTOR FUEL REPROCESSING (J. E. Savolainen)

5.1 Dissolution of PWR Fuel Into H_2SO_4 (A. H. Kibbey)

The dissolution of zirconium or Zircaloy-2 into sulfuric acid may be used as a method of decladding fuel elements with UO_2 cores.

A 5.85 g specimen of PWR fuel, i.e., Zircaloy-2 clad UO_2 was dissolved in a large excess ($\sim 1800\%$) of boiling $14\ M\ H_2SO_4$ under reflux. Initially finely divided black Zr metal and free sulfur formed in the dissolver solution. However, at the end of a 4.5 hour digestion period, all of the finely divided metal had dissolved and the solution was pale yellow-green and water clear; the free sulfur had sublimed off and was solidified in the condenser. Analysis of the solution for Zr and U indicated that the uranium loss to the dissolver solution was $\sim 0.18\%$ of the total uranium. The dissolved cladding contained 0.0356 mg U/ml.

5.2 Hydrochlorination (J. E. Savolainen)

Two irradiated sections of ~~SPR~~ fuel element were hydrochlorinated at $330^\circ C$ to determine the behavior of the fission products. The percent of the fission product activity and the zirconium and uranium remaining with the non-volatile product is listed in the following table. *delete*

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<u>Activity</u>	<u>Run 1</u>	<u>Run 2</u>
Gross β	52	59
Gross γ	23	35
Ru	98	95
Zr	1.7	12
Nb	5	42
Cs	56	41
TRE β	99	99
Sr	100	100
Zr	1.4% (49.5 mg)	7.2% (210 mg)
U	99.8% (37.95 mg)	99.9% (40.42 mg)

A small portion of the fuel specimen of Run No. 2 had not reacted. This incomplete reaction is reflected in the high zirconium and niobium activity retained by the uranium residue.

The results indicate that the only zirconium and niobium fission product decontamination may occur with hydrochlorination. About one half of the long lived cesium activity is sublimed with the zirconium tetrachloride. The presence of the long lived cesium activity will complicate the recovery and reuse of the zirconium tetrachloride.

The plutonium activity was too low to make a reliable analysis. The results indicate that the plutonium remains with the uranium.

6.0 EXCER
(I. R. Higgins)

A flowsheet run has been completed with contaminated synthetic ore leach to produce anhydrous UF_4 . Concentrated brine was used in the anion column without recycle with $CaCl_2$. About 4 lbs of salt was consumed per pound of uranium. The UO_2Cl_2 product averaged 77.9 g U/l and 0.2 M NaCl. Individual samples indicated the U concentration could be 140 g U/l and the low for NaCl in the product was 0.05 M.

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The conversion to UO_2F_2 and the Na removal was done with a fixed bed to save time. The UO_2F_2 product was made 2 M in H_2SO_4 and reduced in the 6 inch cell. The tap density of the final UF_4 product was 3.1.

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

7.1 Protactinium Recovery (A. B. Meservey)

Scavenging of protactinium from periodic samples of Thorex waste by addition of NaOH or HIO_3 to AP have continued to show over 99% removal of the protactinium. Solvent extraction of uranium added to a solution of the scavenger precipitates have been satisfactory. In a second method the uranium was adsorbed on Dowex 50W then eluted with acidified TBP. The uranium was removed leaving the bulk of the fission products on the resin.

7.2 Partitioning of Versene Scrubbed Thorex AU (A. B. Meservey)

Countercurrent batch extraction runs showed no effect on "B" column operation when Versene was used in the AS.

No effect on decontamination in "A" column was noted when Versene was added to the scrub.

R. E. Blanco DEF
R. E. Blanco

D. E. Ferguson
D. E. Ferguson

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