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For The Atomic Energy Commission

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SUMMARY

Homogeneous Reactor Fuel and Blanket Studies

The temperature dependence of the H_2-O_2 combination rate constant for 0.05 m MoO_3 contained in a mixed thorium-uranium oxide slurry was

$$k = 2050 e^{-\frac{1620}{T}}$$

This corresponds to 11 moles of H_2 per liter of slurry at 40°C and a hydrogen partial pressure of 500 psi. The bomb for LITR experiment No. 24 has performed successfully for 100 hr in the laboratory.

Feed Materials

Metallex

The relationship between the free voidage fraction of sintered thorium metal and metal quality is being determined.

Excer

A decontamination run has been completed using the NaCl-water flowsheet and a UF_4 sample submitted for analysis.

Heterogeneous Reactor Processing

The hydrochlorination rate of 2% Zr-U alloy increased from 0.2 to 0.6 mg/min/cm² as the temperature increased from 300 to 350°C.

Ferric ions complex chloride ions and retard the removal of the chlorides from nitric acid by distillation. The removal of hydrochloric acid by distillation is enhanced by the presence of sulfate ions.

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

1.1 Gas Recombination (L. E. Morse)

Measurement of the combination rate of stoichiometric H_2 and O_2 mixtures by slurry containing 0.05 m MoO_3 as a function of temperature were completed. The slurry used was 1000 g Th/kg H_2O prepared from 900°C recalcined D-16 oxide containing 0.5% U. For the slurry as prepared the reaction rate for stoichiometric gas mixture became explosively fast above 268°C while at 250°C the reaction rate was equivalent to the consumption of 2.8 moles H_2 per hour per liter of slurry at a partial pressure of 500 psi H_2 .

Treatment with hydrogen (1000 psi at 25°C) for 1.8 hr at 274°C greatly increased the catalytic activity of the slurry, and subsequent treatment of the slurry with oxygen (500 psi at 25°C) for 1.5 hr at 277°C did not affect this increased activity. The results of measurements of the reaction rate in the temperature range 40-102°C with the hydrogenated and oxygenated slurries were fitted by the least squares relation:

$$k = 2050 e^{-\frac{1620}{T}}$$

where

k = specific reaction rate constant (hours⁻¹)

T = absolute temperature.

The treated slurries were extremely reactive at low temperature having rates equivalent to the consumption of 11 moles H_2 per hr per liter of slurry at 40°C and a partial pressure of 500 psi H_2 and demonstrated resistance to poisoning in contrast to the behavior of palladium. At the highest temperature that it was feasible to make measurements, 101°C, the reaction rate was equivalent to the consumption of 25 moles H_2 per hour per liter of slurry at a partial pressure of 500 psi H_2 .

1.2 Slurry Irradiation Studies (A. R. Jones, N. A. Krohn, W. M. Woods)

The slurry for LITR experiment number 24, 750 g Th/kg H₂O slurry of mixed ThO₂ and 93% enriched U²³⁵O₃ plus 0.15 m MoO₃ catalyst, was prepared from coprecipitated Th and U oxalates which were calcined at 900°C. The uranium concentration is 0.5 mole percent. The experiment is ready for insertion on 5/15/56. The solenoid windings were prepared from sodium silicate (Sauereisen thinner No. 14) coated double-glass insulated aluminum wire, and coils were impregnated heavily with Sauereisen No. 1. In the laboratory the bomb has stirred without incident for 100 hr. The viscosity has remained constant at 9 cstk, and the windings show no deterioration.

2.0 FEED MATERIALS (O. C. Dean)

2.1 Metallex (O. C. Dean)

2.1.1 The Quality of Metallex Thorium Metal

The determination of "free voidage" or atmosphere-connected voidage of sintered thorium metal has been proposed as a quantitative measure of its quality. (See Chemical Development Status Report for Week Ending May 4, 1956). It is reasoned that minimization of this free voidage may produce sound, oxide-free metal which will result in a better rolled, extruded or arc-melted final product. The validity of the proposed method is under test, using oxide content of sintered metal, hardness and density of a cold-upset specimen and metallographic examination as criteria. It is proposed that the free voidage determination, if its validity is proven, be used in optimizing the variables of sintering, washing and reduction.

Eighteen sintered metal samples are under test at present. The free voidage fraction in these samples has ranged from 7.47 to 47.6%. Table 1 shows how some free voidage fraction determinations (expressed as percents) may be related to reduction and washing variables. It is known that thorium amalgams produced at higher temperatures are reactive to water and oxygen, and this is reflected in increased free voidage. The voidage test shows

that water removal by vacuum-drying is more effective than by methanol-rinsing.

Table 1

Sample Thorium Metal	Treatment History	% Atmosphere-connected voidage
TAS-12-2	Reduced at 130°C washed in 1 N HCl + H ₂ O rinsed, argon- sparged H ₂ O, pressed at 1000 psi, sintered.	13.2
TAS-12-3	Reduced at 130°C, washed in 1 N HCl + H ₂ O, rinsed in de- oxygenated methanol, pressed at 1000 psi, sintered.	11.7
TAS-12-1	Reduced at 130°C, washed in 1 N HCl + H ₂ O, vacuum-dried pressed, sintered.	7.47
TAS-13-2	Reduced 200°C washed in 1 N HCl + H ₂ O rinsed with argon- sparged H ₂ O, pressed, sintered.	35.4
TAS-13-1	Reduced 200°C washed in 1 N HCl + H ₂ O, rinsed with oxygen- free methanol, pressed, sintered.	38.1
TAS-13-3	Reduced 200°C washed in 1 N HCl + H ₂ O, vacuum-dried, pressed, sintered.	30.2

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3.0 EXCER (I. R. Higgins)

A product solution of UO_2Cl_2 solution from the 2 inch continuous contactor, using a synthetic contaminated ore leach and the NaCl -water elution flowsheet, was processed in a fixed bed ion exchange system in order to get a sample through electrolysis without delay. The UO_2Cl_2 contactor product, ~ 45 g U/l, was high in NaCl , 1.4 M, because of experimentation with instrument controls. After conversion to UO_2F_2 on Dowex 50 the 84 g U/l product contained 3.5 g/l Na and 0.24 g/l of Ca. After treatment of the UO_2F_2 solution with H-form Dowex 50 the Na was reduced to 0.007 g/l and the Ca to 0.12 g/l. After electrolysis and dehydration the UF_4 product had a tap density of 2.3 and was turned in for chemical analysis.

Since the electrolytic cell was running, four feeds were studied to determine if either Ca or Na effected product density. The product from the ion exchange run had a tap density of 2.4 before dehydration. A synthetic pure UO_2F_2 feed gave a density of 1.5. When Ca was added to the synthetic feed to 0.16 g Ca/l the density was 1.6. When NaCl was added to 2 g/l the density was 1.6. The density problem is becoming critical because we have not found the answer yet. The fact that ion exchange feed gave higher density products indicated that contaminants may have been the answer but now Na and Ca have been ruled out. The problem will be given priority and variations in current density and feed concentration tried next.

4.0 HETEROGENEOUS REACTOR PROCESSING (J. E. Savolainen)

6.1 Hydrochlorination (J. E. Savolainen)

The rate of hydrochlorination of 2% Zr-U alloy increases with temperature as is shown in the following table.

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<u>Temperature</u>	<u>Reaction rate, mg/cm² min</u>
300°C	0.172
310-320°C	0.326
350°C	0.645

6.2 Hydrochloric Acid Removal (J. E. Savolainen)

Ferric ions forms complexes with chloride ions and reduce the volatility of hydrochloric acid from solutions of stainless steel dissolved in hydrochloric-nitric acid mixtures. Nickel and chromium, Cr^{+++} , have no deleterious on the vapor liquid equilibrium of the hydrochloric acid.

The presence of sulfate ions reduces the complexing effect of the ferric ion on chlorides, probably by the formation of a more stable complex.

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