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For The Atomic Energy Commission

H. F. Canale
Chief, Declassification Branch

SUMMARY

Feed Materials

Metallex

The water content of the thorium chloride and the concentration of sodium in the amalgam were shown to be significant factors affecting yields in the reduction of ThCl_4 with sodium amalgam.

The use of deoxygenated methanol for washing thorium amalgams produced amalgams containing mercurides of small particle size.

Volatility Studies

The decomposition of UF_6 gas in contact with NaF at 300°C resulted in the weight of the NaF bed increasing at the rate of 0.4% per minute. A rate of 1.7% per minute was observed at 350 and 400°C .

Plutonium Producer Blanket Processing

When UO_2SO_4 preconditioned at 250°C under 100 psi O_2 was used for feed preparation, no plutonium hydrolysis and precipitation was noted when 1.4 m UO_2SO_4 containing less than 25 mg Pu/kg H_2O was heated at 250°C under 100 psi O_2 and 200 psi H_2 . When the initial plutonium concentration was 100 mg/kg H_2O , hydrolysis and precipitation occurred leaving only 4 mg Pu/kg H_2O in solution.

Mass 233 Studies

A flow ratio of aqueous to organic of 1.5 to 1.0 gave satisfactory stripping of thorium and uranium with 9 stages in the Thorex AC-ABC system.

Homogeneous Reactor Fuel and Blanket Studies

A 750 g Th/kg H_2O slurry of thorium-0.5% uranium oxide (U^{235}) which had been calcined at 900°C showed no increase in apparent viscosity after 192 hr irradiation at 300°C and a neutron flux of 3×10^{13} n/cm²/sec. A thorium

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oxide slurry containing 0.075 m molybdenum oxide catalyst activated with hydrogen gave a hydrogen-oxygen combination rate of 30 moles of hydrogen per hour per liter of slurry at 160°C and $P_{H_2} = 500$ psi.

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1.0 FEED MATERIALS (O. C. Dean)

1.1 Metallex (O. C. Dean)

In three laboratory-scale runs, in which dry powdered ThCl_4 was reduced by sodium amalgam, insignificant amounts of thorium quasi-amalgam were produced. Since yields under the reduction conditions employed were usually 70 to 80% of the thorium fed, reasons for the failure were sought. The thorium tetrachloride used in the first run had absorbed sufficient moisture to raise its water content from 0.5% to 1.44% even though it had been stored and sealed in a bottle in a dry box. The amalgam employed was 3.3 M in sodium. In the second run, the water content was found to be 0.75% for sublimed ThCl_4 salt. In the second and third runs, the amalgam used was only 1.0 M in sodium. It had been stored for a period of about 3 months after generation before using.

Two thorium quasi-amalgams, freshly reduced in the laboratory, were washed in methanol, which had had its dissolved oxygen removed by distillation from alkaline pyrogallol and then sparged with anhydrous HCl . The amalgams were then rinsed in deoxygenated methanol. One of the amalgams was pressed at approximately 5 tsi, but extruded from the die. On repressing with the use of felt pads, the compact was retained in the die, but on ejection to the air showed much reactivity. Both amalgams thus washed gave indications of very small particle size. The second amalgam will be pressed under argon. The reason for elimination of water was to determine, by comparison with water-washed amalgams, whether water and dilute acids react with the thorium during washing and storage, producing thorium hydrides which may cause blistering and cracking during the sintering step.

2.0 VOLATILITY STUDIES (G. I. Cathers)

2.1 $\text{UF}_6 \cdot 3\text{NaF}$ Complex Tests (R. L. Jolley)

Considerable decomposition occurred on contacting pure UF_6 gas with NaF

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at 300°C, leading to the NaF increasing in weight at the rate of 0.4% per minute. At 350 and 400°C the rate was 1.7% per minute although this value probably reflects not the initial rate, but rather the limit of decomposition attainable in the system. These results (Table 1) were secured in tests conducted by passing UF₆ gas (100 mole %) through a weighed NaF bed (12-20 mesh) for various times, then evacuating the system to eliminate excess UF₆ and measuring the weight increase in the NaF. Analyses made on the residue for U⁺⁴ and total uranium content were also used in estimating the percentage weight increase. The total uranium content was generally about twice the U⁺⁴ value so that the weight increase could be calculated on the basis that all of the uranium was actually in the U⁺⁵ state. At 300°C two experiments for two different time intervals resulted in about the rate of increase for the weight of the NaF bed. The high weight increase obtained in the two tests for 15 minutes at 350 and 400°C is of the same magnitude as values obtained previously in this temperature range in a static system after 1 hour tests. It is therefore quite possible that realistic rate data will only be obtained when the total weight increase is kept well below 10%.

Table 1

UF₆ Decomposition Tests

Temperature, °C	300	300	350	400
Time, min	15	30	15	15
UF ₆ flow rate, ml/min	---	136	17	16
U ⁺⁴ content in residue, %	2.6	3.7	6.4	6.6
Total U content in residue, %	4.0	6.8	14.3	14.7
Wt. increase (found), %	6.0	11.6	24.7	26.1
Wt. increase (calc. ^a), %	6.0	10.5	24.7	26.0
Wt. increase rate, %/min	0.4	0.35	1.6	1.7

^aCalculated on basis of U⁺⁵ assumption.

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3.0 PLUTONIUM PRODUCER BLANKET PROCESSING (R. E. Leuze)

3.1 Plutonium Hydrolysis and Precipitation (J. M. Chilton)

During the investigation of plutonium adsorption on metals, a number of experiments showed plutonium solubilities in 1.4 m UO_2SO_4 at 250°C considerably greater than 3 mg/kg H_2O . Studies are now in progress to determine the reason for these high solubilities.

A series of experiments were carried out using mixtures of uranyl sulfate as received from Y-12 and uranyl sulfate conditioned by heating at 250°C under 100 psi O_2 . Different ratios of raw and conditioned uranyl sulfate were used to prepare 1.4 m UO_2SO_4 containing about 18 mg Pu/kg H_2O . These solutions were contained in pyrex tubes and heated in an autoclave at 250° under 100 psi O_2 and 200 psi H_2 . The results in Table 2 show that plutonium precipitation occurred as expected in the raw uranyl sulfate. There was no precipitation in the 100% conditioned uranyl sulfate, and partial precipitation occurred in the mixed feeds. A considerable amount of the plutonium in the oxygen conditioned feed was oxidized to Pu VI. This is partly the reason for high plutonium solubility, however, Pu IV solubilities as great as 10 mg/kg H_2O were noted for some of the mixed feeds. It can also be seen from the results in Table 2 that additional precipitation occurred by heating 62 hr instead of 13 hr. It may also be noted that the Pu VI was gradually reduced. However, none of the plutonium contained in the 100% conditioned uranyl sulfate had precipitated in 62 hr.

In a second series of experiments, fully conditioned uranyl sulfate containing various initial plutonium concentrations were used. These solutions, which were 1.4 m UO_2SO_4 and contained from 10 to 100 mg Pu/kg H_2O , were contained in pyrex tubes and heated at 250°C under 100 psi O_2 and 200 psi H_2 . The results in Table 3 show that plutonium did not precipitate unless the initial plutonium concentration was greater than 25 mg/kg H_2O . These high solubilities appear to be almost entirely the result of Pu VI.

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Heating for 62 hr resulted in additional precipitation for solutions containing initial plutonium concentrations of 35-50 mg/kg H_2O .

Table 2

Dependence of Pu Hydrolysis and Precipitation Upon
Uranyl Sulfate Conditioning

Conditions: 1.4 m UO_2SO_4 containing 18 mg Pu/kg H_2O . Heated at $250^\circ C$ under 100 psi O_2 and 200 psi H_2 . UO_2SO_4 conditioned by heating at $250^\circ C$ under 100 psi O_2 .

% of UO_2SO_4 Conditioned	Plutonium in Solution after Heating (mg/kg H_2O)			
	13 hr		62 hr	
	Total	Pu VI	Total	Pu VI
0	4.90	0.97	0.58	.02
5	6.03	0.31	0.67	.03
10	3.34	0.31	0.66	.34
20	8.28	0.52	0.94	.10
40	10.7	0.50	1.41	.57
60	13.7	2.51	2.53	1.25
80	16.9	6.21	6.03	3.11
100	18	12.2	18	9.4

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Table 3

Dependence of Pu Hydrolysis and Precipitation
Upon Initial Pu Concentration

Conditions: 1.4 m UO_2SO_4 containing Pu. Heated at 250°C under
100 psi O_2 and 200 psi H_2 . All UO_2SO_4 preconditioned
at 250°C under 100 psi O_2 .

Feed Pu Concentration mg/kg H_2O	Plutonium in Solution after Heating (mg/kg H_2O)			
	13 hr		62 hr	
	Total	Pu VI	Total	Pu VI
9.88	10.3	9.2	12.8	8.4
22.8	23.4	18.3	23.1	16.9
24.2	22.4	21.0	23.4	17.9
32.5	20.3	21.7	---	---
36.3	24.9	16.2	13.2	8.8
41.6	17.7	14.9	---	---
51.3	7.3	6.6	5.2	4.0
53.0	8.0	3.9	---	---
103.0	3.9	2.8	3.7	3.0

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4.0 MASS 233 STUDIES (R. H. Rainey)

4.1 Thorex Second Cycle Strip Column (A. B. Meservey)

In a series of tests it was demonstrated in the laboratory countercurrent system that uranium and thorium can be stripped from the organic product of the A column with 0.008 M HNO_3 at an aqueous/organic flow ratio of 1.5:1.0. The 9 stage column came to equilibrium after about 5 volume changes. The uranium refluxed in the organic phase of the feed stage at about four times the concentration of uranium in the feed, and in the aqueous phase of the third stage at about twice the concentration of feed. The uranium loss to the organic phase in either stage 5, 7, or 9 was 0.15%, and the thorium loss was 0.006%. With flow ratios of 1.75:1 and 2:1 the uranium refluxing moved closer to the feed plate, the uranium reflux concentration was lower, and equilibrium was established sooner than at the 1.5:1 aqueous/organic flow ratio.

As noted last week, a flow ratio of 1:1 is unworkable. Ratios between 1:1 and 1.5:1 have not yet been investigated.

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

5.1 Thorium Oxide Slurry Irradiation Studies (A. R. Jones, N. A. Krohn)

LITR run number 25 (750 g Th/kg H_2O slurry of mixed ThO_2 and 0.5 mole percent U^{235}O_3 plus 0.15 molal molybdenum oxide catalyst) was made with oxide prepared from coprecipitated thorium and uranium oxalates by calcination at 900°C . Oxygen overpressure of 250 lb at room temperature was added. The experiment was inserted into the reactor on June 12, 1956. Stirring proceeded well for 123 hr, then stopped for a day. The bomb restarted itself and continued operating until removal except for a few hours of erratic behavior. All told, the bomb operated 219 out of 244 hr in-pile and was irradiated at full power for 192 hr. Viscosity readings of 10 amps remained constant.

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5.2 Gas Recombination Studies (L. E. Morse)

The combination rates for stoichiometric H_2 and O_2 mixtures in $900^\circ C$ recalcined D-16 ThO_2-H_2O slurries containing 1000 g Th/kg H_2O and 0.5% U with 0.075 m MoO_3 as catalyst were measured in the range $86-162^\circ C$. Before being used in the recombination experiments the slurry was treated with H_2 (1000 psi at $25^\circ C$) for 1.5 hr at $276^\circ C$. The temperature dependence of the reaction rate followed the relation:

$$k = 3.99 \times 10^3 e^{-1.94 \times 10^3/T}$$

where:

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

T = absolute temperature ($^\circ K$)

At $162^\circ C$ the reaction rate was equivalent to the consumption of 30 moles of H_2 per hour per liter of slurry at a partial pressure of 500 psi H_2 .

Subsequent treatment of the slurry with O_2 (500 psi at $25^\circ C$) for 3 hr at $278^\circ C$ did not materially affect its catalytic activity. After oxygen treatment the reaction rate at $156^\circ C$ was equivalent to the consumption of 30 moles of H_2 per hour per liter of slurry at a partial pressure of 500 psi H_2 .

The slurry was prepared by tumbling the dry ThO_2 , UO_3-H_2O and MoO_3 for 1 hr and then heating the mixture in water for 3 hr at $280^\circ C$ in the presence of oxygen.

R. E. Blanco

D. E. Ferguson

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