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For The Atomic Energy Commission

H. F. Canale
Chief, Declassification Branch

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SUMMARY

Homogeneous Reactor Chemical Processing

The addition of nitric acid to 10.8 M H_2SO_4 at concentrations of 5 and 15% HNO_3 did not inhibit the corrosion of stainless steel.

Iodine in HR fuel solution is converted by gamma radiation to iodate at a rate dependent on radiation intensity.

Neptunium Isolation

Neptunium (IV) can be loaded on Dowex-50 cation resin from 0.5 N H^+ and 0.05 N NH_4SCN while ferric and uranyl thiocyanate complexes are not sorbed.

Aluminum and Np(IV) sorbed on Dowex-50 resin can be separated by elution of the aluminum with 5% NaOH as sodium aluminate.

Mercury Processing Studies

Metallex

Lowering of thorium losses by oxidation in amalgam washing by Mg addition were confirmed. Deleterious effects on metal quality of high magnesium residue in thorium quasi-amalgam were supported by further data.

The results of using hydrazine dihydrochloride in wash solutions to reduce oxidative losses in washing were inconclusive.

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Homogeneous Reactor Fuel and Blanket Studies

A 750 g Th/kg H₂O slurry of the standard oxide was irradiated at 300°C in the LITR for 344 hr with no apparent deterioration. Molybdenum oxide prepared by the thermal decomposition of molybdic-oxalic acid was an effective gas recombination catalyst in thorium oxide slurries. The effect of sulfate additions on the viscosity of the standard slurry is under investigation. The settling rate of 10°C precipitated oxalate increases with a decrease in the rate of reagent addition ($\text{Th}(\text{NO}_3)_4 \text{ aq} \longrightarrow \text{H}_2\text{C}_2\text{O}_4 \text{ aq}$).

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

1.1 Solids Dissolution (W. B. Howerton)

Attempts to inhibit the corrosion of type 347 stainless steel in 10.8 M H_2SO_4 by the addition of HNO_3 were unsuccessful. In one test with 0.8 M HNO_3 in 10.8 M H_2SO_4 , the corrosion rate increased by a factor of 2.5 to 3.0. In a second test with 2.6 M HNO_3 in 10.8 M H_2SO_4 , the corrosion rate was greater by a factor of 1.1 to 1.6. The percentage of solids dissolved was the same with 0.8 M HNO_3 - 10.8 M H_2SO_4 as with 10.8 M H_2SO_4 . The percentage of solids dissolved decreased from 99% with 10.8 M H_2SO_4 to 93% and 94% with 2.6 M HNO_3 - 10.8 M H_2SO_4 .

1.2 Iodine Chemistry (S. Peterson)

On irradiation of simulated fuel solution (UO_2SO_4 at 5 g U/kg water, 0.005 M H_2SO_4 , 0.005 M CuSO_4 , 5×10^{-6} M I_2) by Co^{60} gamma radiation at 100°C, the iodine is converted to iodate at a rate strongly dependent on the radiation intensity.

At a radiation intensity of 8×10^{17} ev/min/g H_2O (2 watts/liter) and with 200 psi of O_2 (measured at 25°C), iodine was oxidized at the initial rate of 8 equivalents per gram-atom per hour, reaching 95% iodate in 0.7 hr. With the same radiation but only atmospheric oxygen, the rate was 4.3 equivalents per gram-atom per hour, reaching 88% iodate in 2.0 hr. At about one-fourth the radiation intensity, and with only atmospheric oxygen, the iodine oxidized 0.4 equivalents per gram-atom per hour, reaching 23% iodine in 4.2 hr.

The most oxidized solution obtained (95% IO_3^-) was reduced only to 85% IO_3^- on heating an additional 16 hr at 100°C without radiation. In the same bomb without radiation, the iodine is converted partially to iodide, and none to iodate, even with 200 psi O_2 for 40 hr.

2.0 NEPTUNIUM ISOLATION (R. E. Leuze, S. S. Kirsliis)

Ferric and uranyl ions may be completely removed from neptunium by sorbing the thiocyanate complexes on anion resin as described previously. It was found that separation can also be made by sorbing Np(IV) on cation resin while the ferric and uranyl thiocyanate complexes do not load.

A solution containing iron, uranium, aluminum, and Np(IV) was made 0.5 N H^+ and 0.05 N NH_4SCN . Upon passing this solution through a Dowex-50 resin column, the Np(IV) and aluminum were sorbed, but the ferric and uranyl thiocyanate complexes passed through the column. The aluminum was then eluted as sodium aluminate with 5% NaOH. The neptunium was eluted with 5 M HCl. Since only small amounts of neptunium were used in these scouting tests, reliable material balances cannot be made. However, indications are that neptunium losses during the initial sorption and during aluminum elution with NaOH are low. The caustic elution did not completely remove the aluminum since about 10 ppm was found in the 5 M HCl eluate.

3.0 MERCURY PROCESSING STUDIES (O. C. Dean)

3.1 Metallex (O. C. Dean)

3.1.1 Evaluation of Magnesium as an Amalgam Antioxidant

In three reduction runs using 0.03 wt % Mg after reduction and prior to washing it was confirmed that when dry $ThCl_4$ reduction is carried out at 130°C, and 1700 to 2000 rpm agitation, with 3.4 M Na amalgam, and washing with 3 N aqueous HCl that reduction yields are

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85 to 90% instead of 70 to 75% usual for these conditions when no Mg is used. The percentage of the reduced thorium recovered immediately by filtration or centrifugation is 90 to 97%.

One disadvantage in the use of magnesium is that by the present amalgam washing techniques, i.e., 2 passes with 3 N HCl and 2 passes with water, only 10 to 12% of the magnesium is washed from the amalgam. Approximately 10% remains with the quasi-amalgam and the rest with the amalgam filtrate. The 10% remaining with the quasi represents a magnesium to thorium ratio of 1/287, or 3480 parts magnesium per million of thorium. After sintering, the magnesium residues have ranged from 45 to 1200 ppm, too high to meet specifications. In addition the magnesium, having a boiling point of 1110°C, boils off late in the sintering step. This has increased free voidages from the usual values of ~10% to 25 to 30% in the sintered metal. The oxide in the sintered metal has also increased from ~1% when no Mg is used to 2 to 4%. Efforts will be made to reduce the magnesium content of the quasi-amalgam.

3.1.2 Evaluation of Reducing Agents in the Aqueous Wash as Amalgam Antioxidants

In one dry ThCl_4 reduction run at 130°C, 1700 rpm for 30 minutes, and washing with 2 passes of 3 N HCl and 2 passes of H_2O , 5 g/liter of hydrazine dihydrochloride were added to the wash solution to inhibit amalgam oxidation. The reduction yield was 79% instead of the usual 70 to 75% obtained with the procedure using no reducing agents in the washing solution. The Th recovery was 98% of that reduced. The bulk density of the resulting sintered metal was 8.0, the apparent density 11.5, the free voidage 30% and total voidage 31%. The sintered metal had an inferior appearance, but difficulty in the pressing step caused undue exposure to air and cracking of the cold compact, hence it is not certain that the poor quality of the sinter was related to the use of hydrazine hydrochloride.

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

4.1 Thorium Oxide Slurry Irradiation Studies (N. A. Krohn)

LITR experiment 27, using a 750 g Th/kg H₂O slurry of the "standard oxide," was terminated and removed from the reactor after 385 hr of trouble-free operation at 300°C. The LITR was at full power for 344 hr of this period. The viscosity of the slurry remained constant at approximately 9 cstk. In an out-of-pile control experiment the viscosity was 12.4 cstk after the first 24 hr of operation during which time the viscosity was 9 cstk.

A bomb containing 750 g Th/kg H₂O of a mixed thorium-0.5% uranium (containing 93% enriched uranium) oxide was inserted in the LITR (LITR-28). The oxide was prepared by coprecipitating thorium and enriched uranium oxalates followed by calcination to 800°C. The initial viscosity of the slurry was 13 cstk.

Two preliminary corrosion-erosion tests of 100 hr each were carried out in the dash-pot bombs with water at 300°C. No analytical results have been obtained as yet.

4.2 Gas Recombination Studies (L. E. Morse)

Studies are continuing on the effect of alternative methods of catalyst preparation on the hydrogen-oxygen recombination activity of 1000 g Th/kg H₂O slurries of thorium-0.5% uranium mixed oxide containing 0.05 m molybdenum trioxide catalyst. In this series of experiments the molybdenum trioxide was prepared by calcining molybdic-oxalic acid at 400°C for 16 hr in a covered dish. The dry slurry solids were mixed with the catalyst and then suspended in water. Before the slurry was used in the recombination experiments, it was heated under an oxygen partial pressure (300 psi at room temperature) at 280°C for 1-1/2 hr.

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The catalytic activity of the slurry as prepared was not significantly different than that of the slurry containing MoO_3 prepared by calcining ammonium paramolybdate at 480°C . Reaction rates were poorly reproducible and showed a tendency to decrease with succeeding experiments. During the course of one experiment, the reaction which was proceeding at a rate equivalent to the consumption of 6.5 M H_2 per hour per liter of slurry at 269°C and 500 psi H_2 partial pressure suddenly increased to a rate equivalent to the consumption of 43.2 M H_2 per hour per liter of slurry at the same H_2 partial pressure. In the following experiment the reaction rate at 268°C was equivalent to the consumption of 4.1 M H_2 per hour per liter of slurry calculated for an H_2 partial pressure of 500 psi. In a third experiment the stoichiometric gas mixture detonated at 261°C when the shaker was restarted after being stopped for 2-3 min.

Treatment of the slurry with hydrogen (1000 psi at 25°C) at 278°C for 1.6 hr greatly increased the catalytic activity of the slurry for the reaction of the stoichiometric gas mixture. The reaction rate at 180°C was equivalent to the consumption of 28.8 M H_2 per hour per liter of slurry at a partial pressure of 500 psi H_2 . Detonation of the gas mixture occurred when the temperature reached 182°C .

Subsequent treatment of the slurry with oxygen (500 psi at 25°C) at 278°C for 3 hr did not affect the reactivity of the slurry. Detonations occurred in the region about 165°C but reaction rates below this temperature were compatible with the results obtained with the hydrogen treated slurry.

4.3 Slurry Viscosity Measurements (N. A. Krohn)

Viscosity measurements were made in the dash-pot bomb on 200A-6 slurry (600 g Th/kg H_2O) containing sulfate, as $\text{Th}(\text{SO}_4)_2$, and as a function of slurry temperature. Results are given in the following table.

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ppm $\text{SO}_4^{=}$ (based on solids)	Viscosity (in centistokes)			
	60-70°C	110-120°C	200-220°C	300°C
0	12.8	12.6	12.2	---
500	13.4	12.2	9.5	8.4
1000	16.5	14.6	13.6	12.7
1500	15.6	15.9	14.2	13.6
2000	18.3	16.8	15.1	15.7
3000	19.6	18.7	18.2	19.1

4.4 Oxide Preparation Studies (C. E. Schilling)

The settling rate of 10°C precipitated thorium oxalate was found to be less dependent on addition rate (total addition time) when 1 M $\text{Th}(\text{NO}_3)_4$ was added to 0.4 M oxalic acid solution than in the case of 0.8 M oxalic acid which was previously reported. After an initial sharp rise in settling rate from 1 in./hr to 40 in./hr for addition times of 9 to 30 min, only a slight increase in settling rate was observed with further increases in addition time.

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1. Aluminum -- Separation
2. Homogeneous Reactor Test -- Fuel Solution Processing
3. Homogeneous Reactor Test -- Gas Disposal
4. Iodine -- Radiation Effects
5. Metallex Process
6. Neptunium -- Separation
7. Thorium Slurries -- Radiation Effects
8. Thorium Slurries -- Viscosity
- 9.

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- Homogeneous Reactor Test -- fuel solution processing
Homogeneous Reactor Test -- gas recombination
Iodine -- radiation effects
Neptunium -- separation from ~~Fe, U, and Al~~ aluminum, iron, uranium
Aluminum -- separation from ~~Neptunium~~ neptunium
Metallex Process -- development
Thorium slurries -- radiation effects
Thorium slurries -- viscosity

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