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SUMMARY

CLASSIFICATION CANCELLED	
DATE	MAR 12 1957
For The Atomic Energy Commission	
J. R. Connelley	
Chief, Declassification Branch	

Volatility Studies

Either calcination of Superex insulation at 1000°C for several hours in the crumbled form, or use of a hot caustic leach appears promising as a method of removing sulfur and preventing the material from producing sulfur embrittlement effects when used on nickel equipment.

Homogeneous Reactor Blanket Processing

When the plutonium concentration in 1.4 m UO_2SO_4 was increased by daily batch additions of plutonium only partial PuO_2 precipitation occurred upon heating after the plutonium concentration was increased to 25.8 mg/kg H_2O .

Pu(IV) in 1.4 m Li_2SO_4 has a strong absorption band at 350 m μ .

The rate of hydrogen and oxygen combination at 250°C and in intimate contact with 1.4 m UO_2SO_4 is slow enough to allow experiments to run for about a day before adding more hydrogen and oxygen.

The rate of HRT core solids dissolution was approximately doubled for every 10°C increase in temperature between 145° and 230°C.

In order to obtain complete dissolution, it was necessary to heat to 220°C.

Zirconium did not hydrolyze and precipitate as ZrO_2 in boiling solutions containing 7.6 molar phosphate or greater. Type 347 stainless steel in this solution showed no corrosion in 24 hr.

Neptunium Isolation

Ferric and uranyl thiocyanate complexes were strongly sorbed on Dowex-1 resin thus separating them completely from neptunium which did not sorb.

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Mercury Processing Studies

Hermex

One hundred ten grams of dense uranium metal were recovered from ~150 grams of Fernald scrap in the new one-kg Hermex furnace.

Metallex

The use of antioxidants in the amalgam washing step increases reduction yields by about 15% but produced undesirable effects in the sintered metal product.

Dissolution Studies

No hydrogen gas was evolved on the dissolution of stainless steel in aqua regia. The NO_2 and Cl_2 content of the off-gas decreased as the dissolution progressed while the NO content increased.

1.0 VOLATILITY STUDIES (G. I. Cathers)

Based on a limited number of tests the sulfur content of Superex insulation is reduced by calcination at 1000°C only if the insulation is in a crumbled form. Some evidence was also obtained that leaching of the sulfur into 0.1 M NaOH was much more effective than leaching with plain water. Two calcination runs were made at 1000°C for 5 hrs after which the calcined material was leached with hot 0.1 M NaOH for 15 min as a standard procedure. Calcined crumbled Superex was found to have 100 ppm SO_4 (on a solid basis) while calcined block Superex had 250 ppm. In one test with uncalcined material, 180 ppm SO_4 was found using a hot 0.1 M NaOH leach. Less than 50 ppm SO_4 was obtained by leaching with hot water or a cold 0.1 M NaOH solution. However, a blank without Superex also gave less than 50 ppm SO_4 . Although more tests would be desirable it is possible that leaching of Superex would be more desirable than calcination as a means of preventing sulfur embrittlement of nickel equipment insulated with this material.

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

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

The experiment in which about 5 mg Pu/kg H_2O /day is added to $1.4 \text{ m UO}_2\text{SO}_4$ contained in titanium was continued. As reported last week, there were no PuO_2 precipitates formed by heating the solution at 250°C after any of the first 4 additions which raised the plutonium concentration to 21.3 mg/kg H_2O . The next addition raised the plutonium concentration to 25.8 mg/kg H_2O . Upon heating to 250°C there was partial precipitation and 22.8 mg/kg H_2O remained in solution. The next addition raised the plutonium concentration to 32.3 mg/kg H_2O , and there was no additional PuO_2 formed when heated to 250°C .

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2.2 Ultraviolet Absorption Spectrum of Pu(IV)

(J. M. Chilton, R. E. Biggers)

Since spectrophotometric methods may be useful for Pu(IV) analysis in plutonium producer blanket solutions a complete spectrum of Pu(IV) in 1.4 $\underline{m}$ Li_2SO_4 containing 4 g U/l was investigated. There is a strong absorption band at 350 $\text{m}\mu$ with an estimated molar extraction coefficient of 650. The strongest band in the visible region has a coefficient of about 55. The usefulness of spectrophotometric methods for small amounts of Pu, ~ 3 mg/l, in concentrated uranyl sulfate, $\sim 1.4 \underline{m}$, has not been determined.

2.3 Gas Recombination (J. M. Chilton)

When 1.4 $\underline{m}$ UO_2SO_4 with an equal volume gas overpressure of 200 psi H_2 and 100 psi O_2 was agitated and heated to 250°C, about 1.7% of the hydrogen and oxygen combined per hour. This is slow enough to carry out experiments for about a day without the addition of more hydrogen or oxygen.

2.4 HRT Solids Dissolution (R. D. Baybarz)

Dissolution of simulated HRT core solids with phosphoric acid at temperatures from 145°C to 240°C indicate that the reaction rate is doubled for each 10°C increase in temperature. To dissolve 98% or more of simulated core solids (containing $\sim 30\%$ ZrO_2) in H_3PO_4 , it required 65 hr at 145°C, 6 hr at 180°C, 1.5 hr at 200°C, and about 10 min at 230°C. In order to dissolve all of the solids, it was necessary to heat to 220°C.

Overheating the phosphoric acid solution of the core solids to 280°C did not affect the stability. At 300°C a slight amount of precipitate (probably ZrO_2) formed. This solid behaved as a colloid and could not be centrifuged out. In all cases the solution was stable over the temperature range 220°C to 280°C.

It was previously reported that zirconium hydrolyzed and precipitated when the phosphoric acid solution was diluted with water to 4 $\underline{M}$ H_3PO_4 and boiled. By diluting with a 20% solution of $(\text{NH}_4)_2\text{SiF}_6$, zirconium was stable

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in the boiling solution. However, this solution is very corrosive. It was also noted that zirconium hydrolysis and precipitation did not occur from boiling solutions containing 7.6 M phosphate or greater. By diluting the phosphoric acid solution with 5.6 M $\text{NH}_4\text{H}_2\text{PO}_4$ to 3 M H_3PO_4 and still maintaining the total phosphate at 7.6 M, zirconium was stable in the boiling solution. This solution has been boiling at 107°C for 3 days with no evidence of ZrO_2 precipitation. A polished coupon of type 347 stainless steel inserted in this solution for 48 hr showed no weight loss. There was no evidence of pitting or intergranular corrosion.

3.0 NEPTUNIUM ISOLATION (S. S. Kirsliis)

About 0.25 g of neptunium-237 was processed through the chloride anion exchange process previously described. Since the neptunium still contained impurities, further purification was obtained by neptunium fluoride precipitation. Results are not yet available.

Scouting tests show that ferric and uranyl ions may be completely removed from neptunium by sorbing the thiocyanate complexes on Dowex-1 resin. Neptunium did not sorb on Dowex-1 resin from dilute acid solutions containing 0.02 to 0.27 M thiocyanate. The ferric and uranyl thiocyanate complexes sorbed strongly in a dark red band and required drastic elution procedures for removal.

4.0 MERCURY PROCESSING STUDIES (O. C. Dean)

4.1 Metallex (O. C. Dean)

4.1.1 Antioxidants in Amalgam Washing

In three dry reduction runs there have been indications that reduction yields of thorium metal could be increased by use of oxidation inhibitors in the washing operation. In one run the product amalgam was washed with methanol which had been sparged with dry HCl and deoxygenated by distilling

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from alkaline pyrogallol in a stream of argon. The reduction yield was 87% of the thorium charged as compared with the usual 70 to 75%. In two runs 0.03 wt. % of magnesium was added to the Hg phase after the reduction step. In both runs the reduction yields were 90%. Addition of Mg to amalgams before reduction did not significantly increase the metal yield.

In runs where methanol was used for washing, the particle size of the mercuride was apparently reduced so that there was difficulty in thorium recovery by filtration and cold pressing. Also the use of methanol increased the free voidage of the sintered metal, which is undesirable. Magnesium tended to remain in the sintered metal to an undesirable extent in spite of washing with 3 N HCl instead of the usual 1 N acid. Sintered metal contained 45 to 1200 ppm Mg, and the quasi-amalgam contained ~12% of the original Mg added. In addition, Mg appeared to induce a factor of 2 higher porosity and a correspondingly high oxide content in the metal sinter, when the amalgam retorted contained 0.0043 g Mg/g Th or more. Magnesium decontamination over the sintering step was 4 to 100 in 4 runs, and the wide variation could not be explained. If Mg is to be used, the amount entering the retorting step will have to be closely controlled.

4.1.2 Effect of Controlling the Rate of Hg Elimination During Sintering

On a second series of retorting runs by Metallurgy, it has been established that slow elimination of mercury between 140 and 225°C while vacuum sintering improves the physical appearance and decreases the free voidage of sintered thorium metal.

4.2 Hermex (E. Sturch)

Approximately 150 grams of FMPC scrap uranium was dissolved in boiling Hg, pressed into small cylinders, furnace above 1200°C for two hours and 110 g of U having a density of ~ 17 was recovered after cooling.

The quasi prepared by dissolution of 150 g of FMPC scrap U was pressed in a 12-die gang press. The 30 cylinders thus formed (1/2" in diameter and 1/2 to 2 inches long) were stacked in the new one-kg capacity furnace. The temp-

erature was raised to 850°C and held there for 12 hr. The temperature was then raised to and kept above 1200°C for 2 hr. The maximum temperature reached was 1350°C. The furnace was cooled slowly and 110 g of dense uranium metal recovered. Analyses of the product uranium have not been completed.

5.0 HEADEND PROCESSING
(J. E. Savolainen)

5.1 Dissolution of Stainless Steel in Aqua Regia (J. E. Savolainen)

Preliminary studies of the off-gas composition from the aqua regia dissolution of stainless steel have been made. The stainless steel was added in small increments to the dissolvent of 3 M HCl and 4 M HNO₃. Gas samples were collected after each increment had dissolved. A blanket gas, CO₂, was used to exclude acid from mixing with the off-gas. The results of the analysis of the gas samples are listed in the following table with the accumulated amount of stainless steel dissolved per liter. No hydrogen was detected in any of the samples. The evolution of NO increases as stainless steel is dissolved, while the evolution of NO₂ and Cl₂ decreases. The evolution of nitrogen seems to increase slightly.

Off-gas Composition on the Dissolution of
Stainless Steel into Aqua Regia

Dissolvent: 3 M HCl, 4 M HNO₃

Grams S.S. Dissolved Per Liter of Solution	Gas Composition Mole Percent			
	NO	NO ₂	Cl ₂	N ₂
10.9	30.0	24.5	32.4	11.3
21.7	32.6	25.7	31.6	10.0
32.4	50.3	21.5	16.4	11.7
53.4	64.0	15.6	6.0	14.2

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1. Separation Processes -- Development

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 Separation processes -- development at ORNL

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