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FROM: R. E. Blanco
D. E. Ferguson

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For The Atomic Energy Commission

H. R. Canale
Chief, Declassification Branch TC

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- 2 -

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SUMMARY

Equipment Decontamination

A piece of 347 stainless steel pipe from an inpile loop containing uranyl sulfate was decontaminated from 30 r/hr to 6 mr/hr for a decontamination factor of 5×10^3 by treatment with a 0.4 M CrSO_4 -0.5 M H_2SO_4 solution for 2 hr at 85°C followed by 10% NaOH -2 1/2% sodium tartrate-2 1/2% H_2O_2 solution for 4 hr. Fission product analysis indicates Zr-Nb is the primary initial contaminant. After treating with chromous sulfate, activity on the pipe was 99% Ru which read 210 mr/hr.

Decontamination of a 347 stainless steel loop used to circulate thorium oxide slurry at Y-12 lowered the activity from about 10^5 to 50 c/m/in² using the chromous sulfate solution followed by the alkaline tartrate peroxide solutions.

Homogeneous Reactor Blanket Processing

Plutonium adsorption from 1.4 M UO_2SO_4 at 250°C was 20 times greater on rolled Zircaloy-2 with a heavy oxide film than on machined Zircaloy-2.

Mass 233 Studies

Over 99% of the protactinium in a Thorex AP solution was scavenged by precipitating the thorium from the solution with iodic acid.

Homogeneous Reactor Chemical Processing

In the temperature range of 275 - 300°C antimony is soluble in 0.02 M UO_2SO_4 , 0.005 M H_2SO_4 to the extent of 20 ± 5 mg Sb/kg H_2O and will therefore be removed by the HRT chemical plant. The reaction between iodine and silver in the vapor phase above simulated reactor fuel solution at 250 - 300°C is reversible. Therefore, silver will not act as a total sink for iodine in reactor fuel processing at elevated temperature.

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Heterogeneous Power Reactor Processing

Electrolytic dissolution of zirconium fuel elements into a $\text{HCl-HNO}_3\text{-HF}$ can be carried out if the F:Zr ratio does not decrease below 2.3-2.6. Below this ratio a portion of the zirconium leaves the anode as finely divided solids and carries insoluble uranium.

Some of the constituents of stainless steel dissolved in aqua-regia retard the distillation of hydrochloric acid when the distillates were 4 to 6 M HNO_3 .

Metallex

Traces of oil seriously interfere with the reduction of dry ThCl_4 by sodium amalgam.

In washing amalgam with 1 N HCl and water in a packed column, the sodium decontamination factor was 592 and that for Zn, Al, Fe and Ni were ~ 1 .

Neptex

The results of pulsed-column tests indicate that the revised flowsheet for Np-237 recovery from K-25 fluorination ash is generally satisfactory. After 12 hr operation, a U/Np separation factor of 1.6×10^4 was achieved with a 93% Np material balance (feed to product). Total Np and U losses were 4.7 and 0.023%, respectively. Buildup of interfacial emulsions were severe; elevated-temperature digestion of the feed will be tested as a cure.

Excer

Five pounds each of two Excer products with tap densities of 2.2 and 3.2 respectively, have been dehydrated to send to Mallinckrodt to be reduced to metal.

Waste Studies

Aluminum nitrate which had been fired to Al_2O_3 at 500°C and ground to < 100 mesh occluded about 30% of the Cs^{137} and Sr^{90} and would not release them for ion exchange when digested either in 0.1 M HNO_3 or 0.1 M NaOH .

1.0 EQUIPMENT DECONTAMINATION (R. E. Leuze)

1.1 Inpile Loop Decontamination (R. D. Baybarz)

Decontamination of a 347 stainless steel inpile loop specimen was accomplished by a chromous sulfate treatment followed by an alkaline-tartrate-peroxide solution. A 2-inch length of 1/2-inch IPS i.d. pipe obtained from inpile loop No. L 411, (in which uranyl sulfate solution was circulated) was sawed in half lengthwise and a "Cutiepie" reading taken at one inch; the activity was 30 r/hr. The pipe was then inserted in 30 cc of a 0.4 M CrSO_4 -0.5 M H_2SO_4 solution at 85°C for two hr. The pipe was then withdrawn from the solution and the activity read 210 mr/hr at 1 inch giving a decontamination factor of 143 for 2 hr contact time. The pipe sample was then treated for 4 hr with a 10% NaOH-2 1/2% sodium tartrate-2 1/2% H_2O_2 solution at 23°C. The sample was then withdrawn and the activity was down to 25 mr/hr at 1 inch giving an additional decontamination factor of 8.4 and an overall factor of 1.2×10^3 . Sawing off a small section (which was burned when cut apart) of the pipe reduced the activity to 6 mr/hr, thus an overall decontamination factor of 5×10^3 was achieved.

Fission product analysis of the solutions indicated again that Zr-Nb was the primary γ contaminant amounting to $\sim 80\%$ with Ru amounting to $\sim 15\%$. The activity which replated on the metal sample from the chromous sulfate solution was 99% Ru and was the activity which gave the pipe the 210 mr/hr reading after the chromous sulfate treatment. However this Ru was easily removed with the alkaline-tartrate-peroxide solution.

1.2 Thorium Oxide Slurry Loop Decontamination (R. D. Baybarz)

Thorium daughters deposited in a stainless steel loop used to circulate ThO_2 slurries at Y-12 were reduced to below machine shop tolerances by treating the loop with chromous sulfate solution followed by an alkaline-tartrate peroxide solution. Initial activity was not read but was estimated

to be about 10^5 c/m/in². The loop was loaded with 1600 ml of 0.4 M CrSO₄-0.5 M H₂SO₄ solution and circulated at 80°C for 2 hr. The loop was then drained, washed with water, and the pump was dismantled for visual inspection. The surfaces were clean of all oxide film and clinging ThO₂. The activity of the loop was down to ~ 250 c/m/in². The loop was reassembled and 1800 cc of a 10% NaOH-2 1/2% sodium tartrate - 2 1/2% H₂O₂ solution inserted and circulated at 23°C for 4 hr.

The activity of the loop (after the alkaline-tartrate-peroxide solution) was lowered to ~ 50 c/m/in². The decontamination was stopped at this point as the activity remaining was believed to be below shop tolerances. Since the initial activity level was not accurately determined, the overall decontamination factor is now known; however, it was estimated to be greater than 10^3 .

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

2.1 Plutonium Adsorption on Metals (J. M. Chilton)

Plutonium adsorption on metal discs of titanium and Zircaloy-2 stamped from rolled sheets was different than on discs machined from rods. This was apparently the result of differences in the oxide film on the metal surfaces. Surfaces with the heaviest oxide film adsorbed the most plutonium.

Visual examination of the discs under magnifications ranging from 80x to 480x showed that the rolled titanium was smoother and had less oxide coating than the machined titanium. On the other hand, the rolled Zircaloy-2 was covered with a much thicker coat of oxide than machined discs. These discs were exposed for 15 hr at 250°C to 1.4 M UO₂SO₄ containing 7.3 mg Pu/kg H₂O under 90 psi O₂ and 180 psi H₂. Plutonium adsorption was 3.77 μ g/cm² in the rolled Zircaloy-2 and 0.18 μ g/cm² in the machined Zircaloy-2. Plutonium adsorption was 0.07 μ g/cm² on the rolled titanium and 0.18 μ g/cm² on the machined titanium, a factor of 2.5 greater. In a duplicate test using 1.4 M UO₂SO₄ containing 12 mg Pu/kg H₂O, adsorption was 0.09 μ g/cm².

on rolled titanium and $0.30 \mu \text{ g/cm}^2$ on machined titanium.

3.0 MASS 233 STUDIES (R. H. Rainey)

3.1 Protactinium Recovery (R. C. Lovelace)

Over 99% of the protactinium in a Thorex AP solution was scavenged by precipitating the thorium in the solution with iodic acid. A 50 ml sample of Thorex AP from the processing of long cooled thorium slugs was made 0.1 M iodic acid, stirred 30 minutes then centrifuged. Analysis of the precipitate in 6 ml of HCl showed 5.17 mg Th per ml.

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

4.1 Fission Product Chemistry (R. A. McNees)

Experiments to determine the behavior of antimony in simulated reactor fuel at temperatures of $275\text{--}300^\circ\text{C}$ have shown its solubility to be 20 ± 5 mg Sb/kg H_2O . These data were obtained by suspending known concentrations partially hydrolyzed antimony sulfate traced with Sb-124 in $0.02 \text{ M } \text{UO}_2\text{SO}_4$, $0.005 \text{ M } \text{H}_2\text{SO}_4$, heating to the desired temperature and filtering through sintered platinum. The data thus far obtained do not permit a determination of the dependence of solubility on temperature and nothing is known about the composition of the solid product, but these data do show that antimony will be removed in the HRT chemical plant.

4.2 Iodine Chemistry (S. Peterson)

The absorption of iodine by silver from the vapor phase above uranyl sulfate solutions is reversible at $250\text{--}300^\circ\text{C}$. Experiments in which active iodine was initially in the silver phase showed transfer of iodine activity to the liquid phase under conditions such that transport through the vapor phase was the only possible route. Therefore, silver will not act as an

irreversible "sink" for iodine in reactor fuel processing.

5.0 HETEROGENEOUS POWER REACTOR PROCESSING (J. E. Savolainen)

5.1 Anodic Dissolution of STR Fuel (A. H. Kibbey)

Anodic dissolutions of STR fuel were made using various concentrations of HCl-HNO₃-HF solutions as the electrolytes. A current of 4 amperes was maintained throughout the dissolution until upon approach to completion of the dissolution, the current flow gradually dropped to zero. A F:Zr mole ratio of 2.3-2.6:1 was sufficient to prevent formation of finely divided zirconium residue in electrolytes containing 5 M HCl-5 M HNO₃ or 8 M HCl-5.3 M HNO₃, with final zirconium concentrations of about 0.7 M being obtained. When the F:Zr mole ratio was reduced to 1.3-1.4:1 in the 8 M HCl-5.3 M HNO₃ electrolyte solution, 2.65% of the total Zr removed from the anode appeared as finely divided black solids which contained 0.93% of the total uranium present. This is a prohibitive loss figure for enriched uranium systems. The need for at least 1.75 M HF in aqua regia systems containing at least 5 M HCl and 5 M HNO₃ in order to reduce U losses to the 0.1% specification makes this anodic dissolution method appear unattractive. Furthermore, the solids obtained at lower HCl, HNO₃ and HF-concentrations were found to be of an explosive nature--such solids were also formed in 3 M HCl solution containing about 0.15 M HF in the absence of HNO₃.

5.2 Distillation of Hydrochloric Acid from Dissolver Solutions (J. E. Savolainen)

The distillation of hydrochloric acid from a solution of stainless steel dissolved into aqua-regia showed an erratic behavior at low chloride concentrations. Four different distillations were made in which 4 to 6 M nitric acid solution was added to the still at the same rate at which the distillate was obtained. In all cases, the ratio of the relative volatility of the hydrochloric to that of the nitric acid decreased abruptly to a value below one when a low chloride concentration was reached. The conditions at which this occurred varied in each of the cases.

This behavior may be caused by the formation of complexes by the chlorides with the constituents of the stainless steel, presumably the chromic ions.

6.0 FEED MATERIALS (O. C. Dean)

6.1 Metallex (O. C. Dean)

6.1.1 Reduction

In two runs, reducing dry ThCl_4 with sodium amalgam, a slight amount of oil leakage from one of the bearings reduced throrium recoveries by 20 and 70%, respectively below that expected for the conditions of the run.

6.1.2 Washing Amalgam

Sodium amalgam, spiked with 341 ppm Zn, 210 ppm Al, 265 ppm Ni and 274 ppm Fe was washed in the 6-inch glass bead-packed washing column. Two hundred ml of the amalgam was passed five times through the spray head and over the packing countercurrent to a flow of 1 N HCl and three times with argon-sparged distilled water. The amalgam flow rate was $2.6 \text{ ml/cm}^2/\text{min}$ and the aqueous rate, $3.6 \text{ ml/cm}^2/\text{min}$. Only sodium was significantly removed from the amalgam. The initial sodium concentration was 4730 ppm and the final, 8 ppm. The decontamination factor was 592. The zinc decontamination factor was 1.27, and the aluminum, nickel and iron were 1.0. Analysis of the aqueous phase revealed nothing but sodium and a trace of zinc.

In the Metallex process it will be necessary to remove the Al, Zn, Fe, Cu and Ni from the ThCl_4 before the reduction step.

7.0 NEPTEx (J. R. Flanary)

7.1 Neptex (J. R. Flanary, J. H. Goode)

Performance tests of the solvent-extraction flowsheet for recovery of

Np-237 from K-25 fluorination ash have been continued at the Bldg. 3550 pulsed-column facility. Previous runs had evidenced relatively poor separation of neptunium from uranium owing to insufficient nitric acid salting strength in the lower (uranium back-extraction) section of B column. Therefore, flowsheet conditions were slightly modified to permit greater extraction and carryover of nitric acid from A to B column. This was done by reducing the relative flow of feed from 17 to 14 ml/min and increasing the scrub nitric acid concentration from 1.6 to 2.5 M. The revised flowsheet is now:

AF/14 ml/min	1.8 <u>M</u> $\text{Al}(\text{NO}_3)_3$, 1 <u>M</u> HNO_3 , 0.01 <u>M</u> Fe^{++} , 50 g U/1, Np-237
AS/4	0.75 <u>M</u> $\text{Al}(\text{NO}_3)_3$, 2.5 <u>M</u> HNO_3 , 0.01 <u>M</u> Fe^{++}
AX/25	15% TBP in oleum-treated Amsco
BX/7	0.5 <u>M</u> HNO_3
BS/12	15% TBP in oleum-treated Amsco
CX/37	0.01 <u>M</u> HNO_3

Before startup, the B column was filled with 1 M nitric acid, approximately the equilibrium aqueous phase salting strength in the lower section, to hasten the approach to steady-state with respect to uranium/neptunium partition. After six hours operation, end streams were sampled and analyzed. Neptunium extraction and partition losses were 1.2 and 1.8%, respectively, and the neptunium material balance (feed to product) was only 79%, indicating that steady state was not approached. After 12 hours operation, neptunium extraction and partition losses were 3.7 and 1%, respectively, and the material balance was 93%. This balance is probably satisfactory considering the limits of analytical error. Uranium losses were quite low, totaling 0.023% for the cycle. The neptunium product stream contained 0.003 mg Np/ml and 0.006 mg U/ml. This represents a U/Np separation factor of 1.6×10^4 achieved with the flowsheet by pulsed-column operation.

At this point the run was terminated owing to intolerable buildup of emulsion layers at the A and B column interfaces. Future runs will be conducted with feed treated by digestion at elevated temperature on the

premise that colloidal silica is causing the emulsion difficulties.

8.0 EXCER
(I. R. Higgins)

Five pounds each of two Excer products, one tap density 2.2 and the other 3.2, have been dehydrated to send to Mallinckrodt to be reduced to metal.

The 2-inch contactor is presently being run with a synthetic contaminated ore leach using the 5 M NaCl-water elution flowsheet. The product will be run through Excer to determine overall decontamination.

9.0 ION EXCHANGE STUDIES
(I. R. Higgins)

I. R. Higgins, C. W. Hancher, and E. J. Parsi visited Dow Chemical Company at Midland and Illinois Water Treatment Company at Rockford, Ill. Dow has a 30-inch diameter Higgins contactor on test for Ion Exclusion. The Illinois Water Treatment Company was interested in the 12-inch diameter ore contactor to the extent that they may find a place to test it and give some support.

10.0 WASTE STUDIES
(I. R. Higgins)

Aluminum nitrate which had been fired to Al_2O_3 at 500°C and ground to ≤ 100 mesh occluded about 30% of the Cs^{137} and Sr^{90} and would not release them for ion exchange when digested either in 0.1 M HNO_3 or 0.1 M NaOH . The ion exchange treatment of Al_2O_3 slurry was a proposed alternate to diban ion exchange. It was attractive because both aluminum competition for the resin, and chemical costs for aluminum scrubbing would practically be eliminated.

R. E. Blanco

D. E. Ferguson

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