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For The Atomic Energy Commission

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Chief, Declassification Branch TC

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SUMMARY

Fluorox

Calcium fluosilicate was volatilized during hydrochlorination and reduction of ore concentrate-starch pellets.

Excer

The cation exchange step used to convert UO_2Cl_2 to UO_2F_2 unexpectedly eliminated a large fraction of the iron apparently as the chloride anion complex.

Feed Materials - Hermex

Metal recovered from Fernald scrap by the Hermex process met current U specifications for all process impurities except for copper, silicon and boron. Dissolution in Pyrex apparatus may be the reason for B and Si contamination.

Heterogeneous Processing

The Nb-containing uranium alloys were effectively dissolved in 2 M HCl-5 M HNO_3 . Uranium losses as undissolved solids were less than one percent.

Chlorides were effectively removed from aqua regia solutions of 12% Mo-U PWR fuel element alloy to less than 5 ppm.

Homogeneous Reactor Chemical Processing

The presence of ruthenium in simulated reactor fuel solutions inhibits the transfer of iodine to the vapor phase above those solutions but no other fission or corrosion product tested thus far has such an effect.

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Equipment Decontamination

Decontamination of a 347 stainless steel autoclave liner with a 0.4 M CrSO_4 --0.8 M H_2SO_4 solution gave gross β - γ decontamination factors of 150-300 at 23°C and 14-24 at 85°C. Plutonium removal was greater than 99.5% at 85°C and greater than 95% at 23°C.

Corrosion rates of inconel, nickel and monel in KHF_2 at 250°C were 50, 25, and 13 mpy, respectively. Some pitting was observed on inconel with the average being .004 mm deep. Pitting and intergranular corrosion on nickel and monel were negligible.

Homogeneous Reactor Fuel and Blanket Studies

Some difficulties have been encountered in stirring 1000 g Th per kg H_2O slurries of 900°C calcined oxide containing 0.5 mole % uranium in the dash-pot irradiation bomb. Gas recombination studies with MoO_3 catalyst are continuing. Thorium-uranium and thorium-calcium mixed oxides are being investigated.

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1.0 FLUOROX
(R. G. Wymer)

1.1 Ore Concentrate Studies (L. M. Ferris)

A study of African ore concentrate (containing $\sim 80\%$ UO_3) has been initiated to evaluate the feasibility of using this material as feed for the moving bed reactor. The major impurities in this ore concentrate are shown in the following table.

Impurities in Cal Prods African Ore Concentrate

Si - 1.6%	Mn - 0.35%
C - 0.09%	SO_4^- - 6.17%
Al - 0.34%	H_2O - 4.74%
Ca - 0.60%	NH_4^+ - 1.77%
Mn - 0.35%	

Five grams of ore concentrate-starch pellets contained in a Pt boat were simultaneously reduced and hydrofluorinated by reaction at 500°C for 1 hr and at 700°C for 2 hr. The resulting pellets were dark green (indicative of the presence of UF_4), and occupied a volume which was about $1/5$ that of the original ore concentrate pellets. CaSiF_6 was found at the cool exit-end of the reactor, possibly indicating that it is volatile at the temperatures used.

2.0 EXCER
(I. R. Higgins)

The 2-in. continuous contactor is nearing completion. Until continuous runs can be made all the way from simulated ore leach to purified UF_4 , flowsheet variations are being tested on fixed beds.

Fission product analyses are not complete but the decontamination factor for U from TRE was 153 by anion exchange and $> 10^4$ by cation to

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give a total of $>1.5 \times 10^6$. The D.F. for Ru was 75 for anion and 38 for cation exchange for a total of 2800.

The cation exchange step, used to convert UO_2Cl_2 to UO_2F_2 , is being checked for decontamination of Fe, Al, and Na. The addition of 0.1 N oxalic acid to the feed, which had been found effective for Zr and Nb, gave a D.F. of 15 for Al but none for Fe^{+3} . The 1 M HCl, used for Na elution, unexpectedly removed a large fraction of the Fe^{+3} , apparently as a chloride anion complex. The separation factor for Na and U on Dowex 50W-12% 50-100 mesh is 2.7 in 1 M HCl and almost nil for IR-120. Another approach to Na separation is to leave it on the resin and selectively remove U with HF. A D.F. of 130 has been demonstrated for this scheme.

An electrolysis run has been made to prepare $\text{UF}_4 \cdot 3/4\text{H}_2\text{O}$ slurry for Unit Operations decantation and filtration tests. For the first stage, a current efficiency of 87% was obtained for 75% reduction and 81% efficiency for 92% reduction.

2.1 Ore Treatment (I. R. Higgins) .

Vanadium occurs in many U ores in about equal concentration. Since the V has been dissolved, a simple recovery step is desirable to defray U processing costs. Vanadium is reduced to V^{+4} to prevent its sorption on the anion resin with uranium. For vanadium, a cation exchange recovery was considered. From a Utex leach, V was concentrated on a cation resin by a factor greater than 10 with a recovery of 97% and eluted with concentrated brine. Iron was sorbed stronger than V, and V stronger than Al. This flowsheet is a simple recovery-concentration step but delivers a highly contaminated product.

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3.0 FEED MATERIALS
(O. C. Dean)

3.1 Hermex - Purification of Fernald Scrap Uranium (B. H. Morrison)

Fernald scrap uranium was dissolved in boiling (356°C) mercury at a rate of 29 grams in 2 hr. Spectrographic analysis of the metallic uranium recovered from the unwashed uranium quasi-amalgam indicated ~ 5 ppm of Al, B, Ca, Fe and Ni, 15 ppm of Cu, and 150 ppm of Si. The uranium met all current specifications except those for B, Si, and Cu. Probably the high B and Si content is due to the glass equipment used.

A 74 g piece of uncleaned Fernald scrap uranium was placed in the Hermex continuous dissolver and extracted for two 60-minute-periods with 200 ml portions of boiling Hg. Approximately 29 g of uranium dissolved from the scrap at an average rate of 250 mg/min. The surface area could not be measured because of the sample irregularity so the dissolution rate could not be calculated in terms of mg $\text{U}/\text{cm}^2/\text{min}$.

The dilute uranium amalgam was filtered at 350°C through a sintered glass disc fused to the bottom of the dissolver vessel. This hot-filtered amalgam was cooled to 25°C and again vacuum filtered. The purpose of the hot filtration was to retain insoluble oxides, carbides and salts in the dissolver vessel. The cold filtration retained 4% uranium quasi-amalgam on the filter and permitted the uranium-free mercury filtrate to be recirculated to the dissolver vessel. The uranium quasi-amalgam was not washed but was loaded into a ZrO_2 crucible and slowly heated to 1300°C to volatilize off the mercury and melt the uranium. The dense metallic uranium from the furnace operation was analyzed spectrographically. The results are compared with current uranium specifications in the following table.

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Spectrographic Analysis of Uranium

<u>Element</u>	<u>Hermex Metal (ppm)</u>	<u>Typical Biscuit Metal (ppm)</u>	<u>Current Specifications (ppm)</u>
Al	5	< 20	5
B	6	.2	.2
Ca	5	< 5	1
Cu	14	7	1
Fe	7	20	10
Mg	.007	15	1
Mn	.03	8	5
Ni	4	3	3
Si	150	8-40	20

About 9% of the uranium was lost as crud in the dissolver vessel. This high loss was due in part to ionic uranium compounds initially present in the scrap metal.

4.0 HETEROGENEOUS PROCESSING
(J. E. Savolainen)

4.1 Dissolution of U-Nb Alloys in Aqua Regia (A. H. Kibbey)

Alloys containing 2, 5 and 15% Nb by weight were dissolved in 2 M HCl--5 M HNO₃ solution. The insoluble grey-black residues were removed and washed by centrifugation. The supernates and residues were analyzed for uranium. The results showed that uranium retention in the Nb residue ranged from about 0.2 to 1.0%. The data are summarized in the table below:

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Dissolution of U-Nb Alloys in Aqua Regia

<u>% Nb in Alloy</u>	<u>% U Retained in Solid Residue</u>
2	0.16
5	0.98
15	0.57

4.2 Chloride Removal from U-Mo Dissolution (M. L. Hyman)

Chloride removal from a dissolving of 12% Mo-U alloy PWR fuel element cores in aqua regia was demonstrated. The dissolver solution in which the molybdic acid had precipitated was treated with nitric acid to bring the solution to 5.4 N H^+ and 2.14 N Cl^- . A 1.5 in. diam. refluxing column packed with glass Raschig rings (6 x 6 x 1 mm wall) was used with a reflux ratio of about 5. The chlorides in the residue were reduced to less than 5 ppm, and the acidity was 2.4 N H^+ . The gross removal of the chlorides appeared to be by oxidation.

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

5.1 Iodine Chemistry (S. Peterson)

The effect of fission and corrosion product elements on the behavior of iodine in simulated reactor fuel solution has been traced to ruthenium. In a series of experiments it was found that transfer of iodine from the aqueous fuel solution to a silvered alundum pellet in the gas phase above the liquid phase was inhibited by the presence in the aqueous phase of simulated fission and corrosion product elements. In order to identify the offending element, samples containing various combinations of such elements were compared. It was found that the

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presence of rare earths, alkaline earths, iron, chromium, nickel, zirconium and molybdenum was without effect on the transfer of iodine from the liquid to a silvered pellet. Addition of ruthenium to any combination of the above elements drastically curtailed the transfer of iodine to the pellet. Additional experiments demonstrated that iodine adsorbed in a silver-impregnated alundum pellet would be transferred to an aqueous fuel phase which contained ruthenium.

It was also found that stainless steel test specimens present in the aqueous phase during the above experiments aided in the transfer of iodine to the silvered pellet but did not themselves adsorb any iodine activity.

6.0 EQUIPMENT DECONTAMINATION
(R. E. Leuze)

6.1 Homogeneous Reactor Equipment (R. D. Baybarz)

Decontamination of a type 347 stainless steel autoclave liner (used for plutonium and fission product deposition on metal samples from uranyl sulfate solutions at 250-300°C) with chromous sulfate solution was more effective at 23°C than at 85°C. The stainless steel had a heavy oxide film about 8 to 10 mils thick. The liner was cut into several pieces which were then placed in 0.4 M CrSO₄--0.8 M H₂SO₄ for 2 hr. Decontamination results are shown in the table below. Decontamination factors at 23°C were 150-300 and at 85°C were 14-24.

At 85°C the oxide film was completely dissolved, placing all the plutonium and fission products in solution. Apparently, the fission products then replated on the metal samples. Since the metal was then free of oxide film, the remainder of the activity was effectively removed by alkaline-tartrate-peroxide solution.

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Decontamination of Type 347 Stainless Steel

Contamination: deposition from UO_2SO_4 at 250-300°C

Decontamination: 0.4 M CrSO_4 -- 0.8 M H_2SO_4 for 2 hr

Temperature (°C)	Cutie-Pie Readings		Decontamination Factor	Pu Removed (%)
	Initial mr/hr	Final mr/hr		
85	500	35	14	99.98
85	550	34	16	99.98
85	800	34	24	99.96
23	750	5	150	99.71
23	1000	4	250	99.46
23	900	3	300	97.47

In 2 hr, the activity of the first three samples in the above table was reduced to 2-3 mr/hr with the 10% NaOH-2 1/2% Na tartrate-2 1/2% H_2O_2 solution, giving an overall decontamination factor of greater than 200.

At 23°C the oxide film was not dissolved but rather was reduced to a loosely held oxide. The oxide was washed off with a stream of water and became a semi-colloidal suspension. As the oxide was not completely dissolved, the quantity of fission products in solution was small; thus, replating of fission products was not noticeable. Twelve hours contact time was required for complete dissolution of the oxide at 23°C.

Plutonium removal was complete. Plutonium concentrations as high as 15 $\mu\text{g}/\text{cm}^2$ were reduced to less than 0.002 $\mu\text{g}/\text{cm}^2$. In all cases greater than 99.5% of the plutonium was removed at 85°C and

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greater than 95% at 23°C. In several cases plutonium decontamination factors of 10^5 were obtained.

Although greater β - γ decontamination factors were obtained at 23°C than at 85°C, the complete dissolution at 85°C followed by alkaline-tartrate-peroxide will give a more efficient decontamination of actual process equipment than removal of the semi-colloidal particles resulting from defilming at 23°C.

6.2 Volatility Equipment Decontamination (R. D. Baybarz)

It was previously reported that molten KHF_2 at 250°C readily removes the remaining NaF-ZrF_4 fused salt clinging to nickel reactor walls. Corrosion studies of the KHF_2 at 250°C gave low corrosion rates for nickel, inconel, and monel. Corrosion rates obtained after 155 hr contact time were 50, 25, and 13 mpy for inconel, nickel and monel, respectively. No concentrated corrosive attack was noted at the vapor-molten salt interphase. The samples were examined under a 500X microscope for pitting and intergranular corrosion. The inconel sample showed some pitting with the average being .004 mm deep. The remainder of the corrosion seemed to be of a uniform surface removal. Pitting and intergranular corrosion on nickel were slight, and the monel showed no pitting.

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

7.1 Plutonium Hydrolysis (J. M. Chilton)

A 1.4 M UO_2SO_4 solution containing 14 mg Pu/kg H_2O was heated in a Teflon lined autoclave at 250°C for 72 hr with only an air overpressure. The plutonium remained in solution and 98% was oxidized to Pu(VI). In all previous tests using metal or glass equipment at these conditions, the plutonium remained in the reduced

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state and precipitated as PuO_2 with 1-3 mg Pu/kg H_2O remaining in solution. Owing to these results and to the possibility of fluoride contamination, Teflon will not be used.

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

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

Some difficulty has been experienced recently in attempting to stir in the dash-pot irradiation bomb (both in and out of pile) 1000 g Th per kg H_2O slurries of thorium oxide containing 0.5 mole % of enriched uranium. The slurry oxide was prepared by autoclaving at 300°C the D-16 oxide (650°C fired) with 0.5 mole % of the UO_3 as an aqueous slurry and refiring the resulting mixed oxide at 900°C . One thousand parts per million of PdO (based on the ThO_2) was added to each slurry. In previous experiments with mixed oxides containing natural uranium and with some containing enriched uranium, prepared as above, no stirring difficulties had been encountered. The preparation method is being investigated to determine the cause of the recent difficulties. It should be pointed out, however, that 1000 g Th per kg H_2O is probably very close to the upper limit of slurry concentration that the dash-pot bomb can stir successfully.

8.2 Gas Recombination Studies (L. E. Morse)

The effect of slurry concentration on hydrogen-oxygen recombination by MoO_3 catalyst is being investigated. In a slurry of 900°C calcined thorium-uranium oxide (0.5% U) containing 0.1 m MoO_3 and a slurry concentration of 1000 g Th per kg H_2O , the recombination rate was 0.8 moles of H_2 per hour per liter of slurry at 276°C and a hydrogen partial pressure of 500 psi. With 0.15 m MoO_3 the rate was 8.6 moles of H_2 per hour under the same conditions. The slurry

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was prepared by tumbling a dry mixture of 900°C calcined $\text{ThO}_2\text{-UO}_3\cdot\text{H}_2\text{O}$ and MoO_3 for several hours and then heating an aqueous slurry of the mixture for 3 hr at 280°C in the presence of oxygen. In previous experiments 0.1 m MoO_3 in a slurry of the 900°C calcined oxide containing 660 g Th per kg H_2O , but no UO_3 , recombined 20-25 moles of H_2 per hour per liter of slurry at 250°C and $P_{\text{H}_2} = 500$ psi.

8.3 Mixed Oxide Studies (E. V. Jones, C. E. Schilling)

The mixed oxides prepared by the coprecipitation of thorium and uranous oxalates at 25°C and subsequent thermal decomposition at 300-500°C showed no change in average particle size on reheating at 650°C and then at 800°C. The oxides contained 0.42 and 0.57 mole % U and had average particle sizes of 1.1 μ and 2.1 μ , respectively.

A kilogram of the thorium-uranium oxide containing 0.37 mole % U has been prepared by the coprecipitation technique and multistage calcination ending at 900°C for use in engineering loop tests at Y-12.

The effect on slurry properties of adding 1 mole % CaO to ThO_2 by coprecipitating the oxalates and decomposing to oxide by a multistage firing ending at 900°C and then 1000°C is being investigated. The presence of the Ca lowered the settled densities by 10 to 20%, decreased the hindered settling rates by a factor of 2 to 4, and raised the supernatant pH slightly. After autoclaving a 500 g Th per kg H_2O slurry of the mixed oxide at 300°C for 22 hr, the supernatant contained less than 50 ppm of calcium (less than 6% of total calcium content).

R. E. Blanco

D. E. Ferguson

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