UNCLASSIFIED

OAK RIDGE NATIONAL LABORATORY

Operated By
UNION CARBIDE NUCLEAR COMPANY

UCC

POST OFFICE BOX P
OAK RIDGE, TENNESSEE

EXTERNAL TRANSMITTAL AUTHORIZED

ORNL
CENTRAL FILES NUMBER*W.O. receipt*
CF-56-8-190

DATE: August 23, 1956

SUBJECT: Status Report for Chemical Development
Sections A and B: Week Ending August 17, 1956

TO: F. L. Culler

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

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

Photostat Price \$ 3.30Microfilm Price \$ 2.40

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

UNCLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

UNCLASSIFIED

- 2 -

CLASSIFICATION CANCELLED

DATE MAR 12 1957 *jet*

For The Atomic Energy Commission

H. F. Canale

Chief, Declassification Branch

SUMMARY

Homogeneous Reactor Fuel and Blanket Studies

The settling characteristics of the standard slurry are being determined at slurry temperatures of 100 to 300°C and as a function of sulfate concentration. Thorium-uranium oxides containing 0.5% uranium have been prepared by the hydrothermal decomposition of the nitrate solutions containing 0, 1000, 2000, and 3000 ppm of sulfate. The large scale precipitation of thorium oxalate at 10°C for oxide preparation is still hampered by handling difficulties.

Homogeneous Reactor Blanket Processing

Simulated HRT blanket solids containing about 1% PuO₂ were completely dissolved in phosphoric acid at 220°C, even after the dry solids were heated at 400°C for 1 hr.

Equipment Decontamination

Only a small amount of the oxide corrosion film was dissolved when a 2% H₃PO₃--2% NaH₂PO₂ solution was circulated in a uranyl sulfate corrosion loop for 24 hr at 175°C.

Metallex

X-ray diffraction studies of thorium amalgam showed that the species of thorium mercurides produced are dependent on time and temperature, but not on washing techniques.

UNCLASSIFIED

405 002

DECLASSIFIED

Hermex

Significant decontamination of Fernald scrap U was achieved by Hermex processing. Those impurities which were soluble in mercury were removed to the greatest extent.

Fluorox

Air oxidation of UF_4 increases rapidly as the temperature is increased from 700 to 800°C. Some of the intermediate compounds have been identified.

Darex

Five modified Gillespie stills are expected to be in operation by August 24 for the vapor-liquid equilibrium study. One hydrochloric acid distillation experiment was discontinued because decomposition reactions occurred.

Extraction Reagent Performance

Aqueous washing of highly contaminated Thorex first-cycle solvent with various oxidizing and reducing agents removed essentially none of the activity or yellow discoloration from the solvent. Similar results were obtained by conventional solvent treatment with sodium carbonate and caustic.

Flowsheet Development

Synthetic Purex-type feed solutions (324 g U/l, 28 g SS/l containing from 0.4 to 1.2 M excess nitric acid) representing dissolved

fuel from the Consumers Public Power reactor are quite stable toward precipitation. By contrast, synthetic feeds (324 g U/l, 88 g SS/l containing from 0.4 to 2.0 M excess nitric acid) representing dissolved material from the Detroit Edison axial blanket freeze out at or near room temperature. Such feed, however, can be stabilized by as little as 10% dilution with water if the acidity is held to 0.5 M.

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

1.1 Characterization of Pumped Slurries

The settling characteristics of the standard slurry are being determined as a function of slurry temperature and sulfate concentration. In four successive settling experiments at 100°C the settling rate of a 250 g Th/kg H_2O standard slurry containing no sulfate increased from 0.2 cm/sec to .8 cm/sec while the settling rate of similar slurries containing 1000, 2000, and 3000 ppm remained constant at 0.2 cm/sec. At 200°C in successive experiments (four) the settling rate of the slurry containing the 1000 ppm of sulfate increased from .55 cm/sec to 1.8 cm/sec while the slurries containing the 2000 and 3000 ppm of sulfate gave a constant settling rate of approximately 0.5 cm/sec. The pure slurry at 200°C had a settling rate of 2.3 cm/sec. At 250°C the pure slurry and that containing the 1000 ppm of sulfate settled at 2.8 cm/sec while those containing the 2000 and 3000 ppm of sulfate settled at 1.2 and 0.8 cm/sec, respectively. At 300°C none of the slurries could be suspended in the hindered settling bomb by the pneumatic shaker currently in use.

405 004

DECLASSIFIED

The increase in settling rate observed in successive experiments with the pure slurry at 100°C and with the slurry containing 1000 ppm of sulfate at 200°C are probably due to an enhanced agglomeration characteristic under these conditions resulting in particle growth. At 2000 and 3000 ppm of sulfate particle growth is apparently inhibited by the adsorbed sulfate ion on the slurry solids.

1.2 Thorium-Uranium Oxide Preparation

Thorium-uranium oxides containing 0.5% uranium oxide have been prepared by the hydrothermal decomposition of nitrate solutions containing 0, 1000, 3000, and 5000 ppm of sulfate (based on the thorium oxide). In the absence of sulfate the bulk of the distillate (80%) from the reaction autoclave is 2 N in acid with the final fractions 13-14 N in acid. The sulfate inhibits the acid evolution and the distillate is less than 1 N in acid until the final stages when the acid comes over as a very concentrated solution. While characterization of the oxide product is incomplete, all materials seem suitable for the preparation of aqueous suspensions. The oxide prepared from the solution containing the 3000 ppm of sulfate appears to be of a smaller average particle size and is lighter in color than the other preparations.

1.3 Oxide Preparation (C. E. Schilling)

Two preparations of 10°C thorium oxalate have been made in the pilot plant. The first, when burned to oxide, was found to be unacceptable because of its large average particle size and wide size distribution.

405 005

DECLASSIFIED

The procedure used in the second preparation, 120 lb ThO_2 , was altered to provide a more uniform rate of thorium nitrate addition during the precipitation which, according to laboratory studies, should give a much more uniform particle size. Separation of the solids from the final wash liquid, and drying prior to burning the oxide, continue to be major handling problems. Washing by decantation, the only method currently available, appears to have been facilitated by the more uniform reagent addition rate but is still slow and some losses have been encountered as a result of incomplete settling.

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

2.1 HRT Solids Dissolution (R. D. Baybarz, O. K. Tallent)

Addition of about 1% PuO_2 to the simulated HRT blanket solids did not change the dissolution behavior in concentrated phosphoric acid. The PuO_2 was readily dissolved at 220°C . Upon dilution to 3 M H_3PO_4 after dissolution, the plutonium did not hydrolyze or precipitate but remained stable in solution.

Heating the dry simulated solids at 400°C for 1 hr did not adversely affect their dissolution in H_3PO_4 . Complete dissolution was obtained by adding 1 g of these solids to 10 ml of 85% H_3PO_4 , evaporating to a boiling point of 210°C , and heating at 210°C for 20 min.

3.0 EQUIPMENT DECONTAMINATION (R. E. Leuze)

3.1 Homogeneous Reactor Equipment Decontamination (R. D. Baybarz)

A 2% H_3PO_3 --2% NaH_2PO_2 solution was much less effective for descaling a type 347 stainless steel corrosion loop (used for UO_2SO_4) than was 0.4 M CrSO_4 --0.5 M H_2SO_4 . About 25 l of 2% H_3PO_3 --2% NaH_2PO_2 solution was circulated in a Y-12 corrosion loop for 24 hr at 175°C. Visual inspection showed that only a very small amount of the corrosion oxide film was dissolved. Type 347 stainless steel corrosion specimens showed little corrosion. Complete descaling was previously obtained by this procedure when tested on a small scale. When complete analytical results are available, it may be possible to determine the reason for the difference.

4.0 MERCURY PROCESSING STUDIES (O. C. Dean)

4.1 Metallex (C. P. Johnston)

Previous experiments have indicated that at least two thorium mercuride species are obtained in thorium quasi-amalgam produced by the reduction of ThCl_4 with sodium amalgam. An X-phase, whose composition and structure is unknown, having Bragg angles (2θ) of 28° and 58° are predominant in material produced at 50-150°C, while a ThHg phase is predominant in material produced at temperatures of 250°C and above.

Since this previous work was carried out with material subjected to washing with either aqueous or anhydrous reagents to remove by-products, a new series of experiments was carried out to determine

whether or not the various washing procedures were a factor in the thorium mercuride species produced.

The data in Table 4.1 from these experiments show that time of aging of the amalgam and temperature of preparation are controlling factors of the species produced, while washing technique is not a controlling factor.

Table 4.1

Reduction of ThCl_4 with Na Amalgam			
Temperature (°C)	Washing Procedure	X-phase	ThHg_3 Phase
130	1 N HCl	~95%	~5%
130	Distilled H_2O	~95%	~5%
130 ^a	$\text{HCl-NH}_2\text{NH}_2\text{HCl}$	~95%	~5%
130	Anhydrous alcohol	~95%	~5%
356 ^b	None	~5%	~95%
Dissolution of Thorium in Mercury			
356	None	neg.	99+%
356	Distilled H_2O	neg.	99+%
356	1 N HCl	neg.	99+%

^a Aged one week.

^b Dissolution of thorium metal in boiling mercury. The specimen of thorium mercuride in (b) was aged about 2 weeks while all other samples were 1-3 days aged.

DECLASSIFIED

405 008

4.2 Hermex (E. Sturch)

4.2.1 Processing of Fernald Scrap Uranium

Approximately 150 g of Fernald scrap uranium was dissolved in 10 dissolution passes of 200 ml Hg with a total dissolving time of about 5 hr. Approximately 400 ml of thick quasi was obtained. This quasi was washed in 1 N HCl, dried and cold-pressed into 32 cylinders of 15-18% uranium quasi-amalgam. The cylinders had an average length of 1 in. and a diameter of 1/2 in. These cylinders were fed into the new 1 kg-scale semicontinuous furnace under an argon atmosphere. Most of the mercury was volatilized while the furnace temperature was maintained at 850°C for about 10 hours. The temperature was then raised to 1200°C where it was maintained for more than two hours. The furnace was allowed to cool over a weekend and 110 g of uranium was recovered. The density of the Hermex U was approximately 17.5 g/ml.

Spectrographic analyses of the Fernald and Hermex U (Table 4.2) showed significant removal of most impurities. The increased boron removal and only fair removal of Si is probably due to these metals being introduced from the glass dissolver. The low removal of Fe and Cr and increase in Ni is possibly due to their distillation from the stainless-steel crucible support. As borne out by previous work, Mn and Mg are practically 100% removed.

Table 4.2

Decontamination of Scrap Uranium by the Hermex Process

Impurity	Scrap U (ppm)	Hermex U (ppm)	Impurity	Scrap U (ppm)	Hermex U (ppm)
Al	50	41	Fe	115	96
B	5	9	Mg	8	0.2
Ca	45	10	Mn	16	0.0
Cr	28	21	Ni	0.0	51
Cu	37	5	Si	125	65

5.0 HEAD-END PROCESSING
(J. E. Savolainen)

5.1 Fluorox (L. M. Ferris)

Three preliminary experiments were made to study the oxidation rate of uranium tetrafluoride in dry air at temperatures of 600, 700, and 800°C.

In each experiment, a platinum boat containing about 18 g of UF_4 was placed in a quartz tube and heated to the desired temperature while being flushed with helium. Dry air was then passed over the UF_4 for one hour at a flow rate of about 300 cc/min. After oxidation the UF_4 was allowed to cool in a helium atmosphere.

<u>Temperature</u>	<u>Results after 1 hr of Oxidation</u>	
	<u>UF_4 Weight Loss</u>	<u>U^{+4} Remaining</u>
600°C	0.192%	72.50%
700°C	0.970%	73.71%
800°C	23.5%	61.11%

No comparison of these results to those in dry oxygen have been made as yet.

Uranium pentafluoride (UF_5) has definitely been identified as a product of the reaction of UF_4 with dry oxygen. X-ray analysis showed conclusively that U_2OF_8 , which has chemical and physical properties similar to those of UF_5 , was not isolated from the system.

6.0 DISSOLUTION STUDIES (W. E. Clark)

6.1 Darex Process (A. H. Kibbey)

6.1.1 Liquid-Vapor Equilibria in Aqua Regia Systems

Determinations of liquid-vapor equilibria in aqua regia systems containing stainless steel components are under way using modified Gillespie stills. Difficulties in still operation are being remedied by further design changes, and it is expected that 5 stills will be in operation by August 24. The data obtained to date are not complete enough to allow any definite correlations to be made.

In an experiment on an 80 g/l stainless steel dissolver solution, the chloride concentration was found to decrease from 2.5 M to 1.7 M as the nitrate was increased from 3.5 to 7.5 M in ten steps. In each step 13.5% of the pot volume was distilled and the pot volume was kept constant by the addition of 4.5 M HNO_3 . The distillation was discontinued when decomposition caused entrainment to occur in the still.

7.0 SOLVENT EXTRACTION STUDIES (J. R. Flanary)

7.1 Extraction Reagent Performance (J. H. Goode)

Aliquots of highly-contaminated Thorex first-cycle solvent were contacted for about 10 min with 1/5 volumes of various oxidizing and reducing reagents to determine whether they would remove radiation-induced impurities formed in the solvent; a Redox titration of the solvent with KMnO_4 and $\text{Ce}_2(\text{SO}_4)_3$ had indicated that the organic had a "reducing normality" of about 0.01 M. Washes with 1 M H_2O_2 , ~0.01 M KMnO_4 , and 0.01 M solutions of SnCl_2 , $\text{SnCl}_2 + \text{HCl}$, FeSO_4 , and $\text{NH}_2\text{OH} \cdot \text{H}_2\text{SO}_4$

removed essentially none of the activity or yellow discoloration from the solvent.

Conventional solvent treatment (consecutive 1/5 volume washes of 0.1 M Na_2CO_3 and/or NaOH, H_2O , and HNO_3) had very little effect. The first of two Na_2CO_3 washes formed a slow-settling emulsion during the contact; after the second contact, phase separation improved. No activity was removed by the Na_2CO_3 washes. Subsequent washing with one 1/5 volume of 0.1 M NaOH removed about 30% of the solvent activity; water and HNO_3 washes which followed had no effect.

7.2 Flowsheet Development (J. H. Goode)

Aqua regia dissolution of uranium-stainless steel reactor elements designed for Consumers Public Power and Detroit Edison (axial blanket) is expected to yield solvent-extraction feeds of the Purex type, 324 g U/l and 1 to 2 M HNO_3 , containing 28 and 88 g stainless steel/l, respectively. Accordingly, synthetic feeds of these uranium and stainless steel compositions were prepared to determine solution stability and uranium extraction coefficient as a function of HNO_3 concentration. Table 7.1 summarizes these data. It may be seen that the CPP feed is stable with respect to freezeout at ordinary operating temperatures across the acidity range of 0.4 to 1.2 M; the uranium extraction coefficients are large enough for efficient solvent-extraction. However, all of the DEAB feed solutions precipitated after a few days standing at room temperature. It was necessary, therefore, to reduce the uranium and stainless steel concentrations in these solutions by dilution and redetermine solution stability (Table 7.2).

Thus, it is seen that a stable feed solution can be maintained by as little as 10% dilution if the acidity is held to 0.5 M. With 1.0 M HNO_3 in the feed, a 25% dilution is needed to insure solution

DECLASSIFIED

405 012

stability. With these dilutions, Purex 1A column extraction conditions could be adjusted to accommodate the greater volume of feed without reduction of the uranium mass throughput, it is believed.

Table 7.1

Consumers Public Power

Feed/100 vol: 324 g U/1, 28 g SS/1, HNO_3 as shown
 Scrub/67 vol: 3 M HNO_3
 Solvent/333 vol: 30% TBP³

Feed		Aqueous Phase Acidity (M)	Uranium Extraction Coefficient, O/A
Acidity (M)	Freezing Point (°C)		
0.42	-20	1.52	4.46
1.1	-4	2.0	4.82
1.20	3	2.12	4.88

Detroit Edison Axial Blanket

Feed/100 vol: 324 g U/1, 88 g SS/1, HNO_3 as shown
 Scrub/67 vol: 3 M HNO_3
 Solvent/333 vol: 30% TBP³

Feed		Aqueous Phase Acidity (M)	Uranium Extraction Coefficient, O/A
Acidity (M)	Freezing Point (°C)		
0.45	25	1.54	10.0
1.01	28	1.69	11.8
1.23	28	1.92	15.0
2.0	Insoluble at R.T.		

Table 7.2

Freezing Point of DEAB Feed as a Function of Uranium-
Stainless Steel and HNO₃ Concentrations

Uranium (g/l)	Stainless Steel (g/l)	HNO ₃ (M) ³	Freezing Point (°C)
292	79	0.5	0
		1.0	10
		2.0	20
260	71	0.5	< 0
		1.0	8
		2.0	20
244	66	0.5	< 0
		1.0	0
		2.0	20

R. E. Blanco
R. E. Blanco

D. E. Ferguson
D. E. Ferguson

REB-DEF/jr

405 014

DECLASSIFIED

1-14

0371200330