CONFIDENTIAL COVER SHEET**UNCLASSIFIED**

OAK RIDGE NATIONAL LABORATORY

Operated By

UNION CARBIDE NUCLEAR COMPANY

UCCPOST OFFICE BOX P
OAK RIDGE, TENNESSEE

EXTERNAL TRANSMITTAL AUTHORIZED

ORNL
CENTRAL FILES NUMBER

56-6-103

~~FOR INTERNAL USE ONLY~~

COPY NO. 17

DATE: June 14, 1956

SUBJECT: Chemical Development Status Report
for Week Ending June 8, 1956

TO: F. L. Culler

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

DISTRIBUTION

1. F. L. Culler	24. J. A. McLaren
2. T. A. Arehart	25. R. A. McNees
3. E. D. Arnold	26. R. P. Milford
4. R. E. Blanco	27. W. C. Moore (Y-12)
5. F. R. Bruce	28. E. L. Nicholson
6. W. D. Burch	29. E. O. Nurmi
7. G. I. Cathers	30. S. Peterson
8. O. C. Dean	31. R. H. Rainey
9. W. K. Eister	32. J. T. Roberts
10. H. L. Falkenberry (Y-12)	33. J. E. Savolainen
11. D. E. Ferguson	34. M. J. Skinner
12. J. R. Flanary	35. J. C. Suddath
13. H. E. Goeller	36. J. W. Ullmann
14. A. T. Gresky	37. W. E. Unger
15. C. E. Guthrie	38. C. D. Watson
16. I. R. Higgins	39. M. E. Whatley
17. A. S. Kitzes	40. C. E. Winters
18. R. E. Leuze	41. R. G. Wymer
19. R. B. Lindauer	42-43. Laboratory Records
20. J. T. Long	44. Laboratory Records (RC)
21. R. N. Lyon	45-46. Central Research Library
22-23. J. P. McBride	

Classification cancelled (or changed to) **UNCLASSIFIED**
memo + let J. S. S. cardull
 by authority of *Chief, Tech. Br. OTR 9-26-58*
 by *J. C. Bideman* TIE, date *10-6-58*

NOTICE

RESTRICTED DATA

This document contains Restricted Data as defined in the Atomic Energy Act of 1954. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report.

CONFIDENTIAL COVER SHEET**UNCLASSIFIED**

1 8154

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.

~~CONFIDENTIAL~~

- 2 -

SUMMARY

Volatility Studies

The reaction between F_2 and molten $NaF-ZrF_4-UF_4$ (48-48-4 mole %) at $600^\circ C$ appeared incomplete in batch equilibration tests, possibly as a result of inadequate salt agitation. The gas density of the F_2 employed was determined to be 1.72 g/l in comparison to the ideal value of 1.70.

Homogeneous Reactor Blanket Processing

The amount of plutonium adsorbed on titanium and Zircaloy-2 at $250^\circ C$ from 1.4 m UO_2SO_4 containing 3.8 mg Pu/kg H_2O was not appreciably changed by preconditioning the metal by the proposed HRT method.

Equipment Decontamination

The corrosion film deposited on type 347 stainless steel by uranyl sulfate solution at $250^\circ C$ was dissolved by a solution at $150-200^\circ C$ containing 1% H_3PO_3 and 2% NaH_2PO_2 . Stainless steel from an in-pile loop was decontaminated from 8 r/hr to 250 mr/hr by contacting with this solution at $170^\circ C$ for 18 hr. The phosphorous acid-hypophosphite solution did not dissolve ZrO_2 or PuO_2 and is not as satisfactory for descaling as chromous sulfate in dilute sulfuric acid.

Feed Materials

Metallex

Metal quality appears to be improved by handling and pressing amalgams under an inert atmosphere.

~~CONFIDENTIAL~~

DECLASSIFIED

Heterogeneous Power Reactor Processing

Hydrochlorination

The hydrochlorination rate of 2% Zr-98% U alloy increase from 0.172 mg/cm²·min at 300°C to 0.835 mg/cm²·min at 370°C. The rate can be controlled by controlling the temperature.

The rate of hydrochlorination of a silicon uranium alloy changes slightly with composition and is about 0.1 mg/cm²·min.

Sodium bonded stainless steel clad fuel elements, APDA, dissolve directly into aqua regia. While the sodium reacts violently the amount exposed at any one time is small enough to prevent excessive rates.

Sulfuric acid was used to dissolve zirconium cladding on a laboratory scale.

Fluorox

Hydrogen at 475°C did not remove residual C from UF₄-C pellets contained in a Ni boat.

The specific surface area of UO₂F₂ was found to be much greater than that of UF₄.

Excer

A tap density of 3.1 was obtained for an Excer product starting with synthetic ore leach.

Fused Salt Dissolution

STR dissolution rates in fused NaF-ZrF₄ at 600°C decrease from 7-9 to 0.8-1.0 mg/min·cm² as the ZrF₄ content is increased from 35 to 60 mole %.

~~CONFIDENTIAL~~

- 4 -

1.0 VOLATILITY STUDIES (G. I. Cathers)

1.1 Fused Salt-Fluorination Equilibrium (M. R. Bennett)

Incomplete reaction was obtained in three batch equilibration tests of F_2 with molten $NaF-ZrF_4-UF_4$ (48-48-4 mole %) at $600^\circ C$ apparently due to poor contact between the salt and gas phases. These runs were made in developing a satisfactory test procedure for measuring the fused salt-fluorination equilibrium constant. In the three tests to date, the reactor containing the salt and F_2 gas was maintained for about 2 hr at $600^\circ C$ and at atmospheric pressure by feeding F_2 into the system to make up for any F_2 consumption. Two methods were used in analyzing the gas phase after the equilibration period. In the first run, the test reactor was cooled quickly to $100^\circ C$ and the gas flushed through a NaF bed to trap UF_6 . The amount of UF_6 found in the gas phase corresponded to only 8.7 mole %. Based on previous work, the equilibrium gas should be almost pure UF_6 , i.e., that K_p for the reaction is large. In the next two tests the composition of the gas was determined by density. In both cases the gas appeared to be essentially pure F_2 . Although it seemed improbable that UF_6 redissolved in the molten salt during solidification, gas sampling in the third run was done without prior solidification of the salt phase. The most probable explanation of the small amount of UF_6 found in each run is that there was not enough agitation of the molten salt to insure complete equilibrium with the reacting gas.

The density of the F_2 used in the above work was determined to be 1.72 g/l (S.T.P.) in contrast to the theoretical density of 1.70. The comparison indicates that the F_2 is fairly pure.

~~CONFIDENTIAL~~

DECLASSIFIED

~~CONFIDENTIAL~~

- 5 -

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

2.1 Slurry Irradiation Studies (A. R. Jones, N. A. Krohn)

The bomb testing facility is now in use. Three in-pile bombs have been tested with one failure.

The slurry for LTR experiment number 25, a duplicate of 24, (750 g Th/kg H₂O slurry of mixed ThO₂ and 93.14% enriched U²³⁵O₃, plus 0.15 molal molybdenum oxide catalyst), was prepared from coprecipitated thorium and uranium oxalates which were then calcined to 900°C. The uranium concentration was 0.5 mole %. It will be inserted into the reactor on 6/12/56. A 250 lb overpressure of oxygen will be added at room temperature.

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

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

Preconditioning titanium and Zircaloy-2 by the HRT method had no appreciable effect on the amount of plutonium adsorbed in 195 hr at 250°C from 1.4 M UO₂SO₄ containing 3.8 mg Pu/kg H₂O. This agrees with the results reported last week after a 15 hr contact time.

Titanium and Zircaloy-2 metal disks were preconditioned by washing them in 3% trisodium phosphate solution followed by 5% HNO₃ at room temperature for 24 hr, heating in water at 250°C under 350 psi O₂ for 100 hr, and heating at 250°C in 1.4 M UO₂SO₄ under 350 psi O₂ for 400 hr. Conditioned and unconditioned metal samples were contacted at 250°C with 1.4 M UO₂SO₄ containing 3.8 mg Pu/kg H₂O under 200 psi H₂ and 100 psi O₂ for 195 hr. The average plutonium adsorption on conditioned and unconditioned titanium was 0.068 and 0.085 µg/cm², respectively. Plutonium adsorption on machine buffed Zircaloy-2 was 0.73 µg/cm² for

~~CONFIDENTIAL~~

DECLASSIFIED

~~CONFIDENTIAL~~

- 6 -

unconditioned samples and $0.66 \mu\text{g}/\text{cm}^2$ for conditioned samples. Plutonium adsorption on Zircaloy-2 that had not been buffed was $2.64 \mu\text{g}/\text{cm}^2$ on unconditioned samples and $1.88 \mu\text{g}/\text{cm}^2$ on conditioned samples. Although there appears to be less plutonium adsorbed on the conditioned metals, these differences are less than variations obtained in duplicate tests.

4.0 EQUIPMENT DECONTAMINATION (R. E. Leuze)

4.1 Homogeneous Reactor Equipment (R. D. Baybarz)

The use of phosphites and hypophosphites in combination with phosphorous acid at elevated temperature (150 - 225°C) for the removal of the oxide film deposited on 347 stainless steel from UO_2SO_4 solutions at 250 - 300°C was partially satisfactory.

Molten phosphorous acid removed the oxide film from type 347 stainless steel in ~ 3 hr at 110°C with heavy corrosion of the base metal. Dilution of the phosphorous acid below 25 weight % caused the solution to be completely ineffective even at 250°C for a 48 hr contact time.

A solution containing only 1 weight % H_3PO_3 and 2 weight % NaH_2PO_2 was effective in removing the oxide scale. When this solution was used at 150°C , the oxide film was dissolved leaving the metal clean and free of all adhering oxide after 12-15 hr. However, attempts to dissolve ZrO_2 were unsuccessful in the temperature range 150 - 225°C . A minimum temperature of 150°C is required before iron oxide dissolution begins, and at temperatures in excess of 200°C a secondary oxide film is deposited after removal of the initial corrosion oxide film.

Use of the phosphorous acid-hypophosphite solution for decontamination of in-pile loop specimens was satisfactory. At 170°C two specimens were decontaminated from 8 and 4 r/hr to 250 and 300 mr/hr, respectively, in

~~CONFIDENTIAL~~

DECLASSIFIED

~~CONFIDENTIAL~~

- 7 -

18 hr. The remaining activity was totally ruthenium and was easily removed with alkaline-tartrate-peroxide lowering the activity to 20 and 10 mr/hr, respectively.

The phosphorous acid-hypophosphite solution was not effective for removing PuO_2 from stainless steel.

In static corrosion tests, the corrosion of 347 stainless steel in 1% H_3PO_3 -2% NaH_2PO_2 at 150-180°C was 50-100 mpy. Zirconium and titanium were apparently not corroded by the 1% H_3PO_3 -2% NaH_2PO_2 solution.

The phosphorous acid-sodium hypophosphite solution gave good decontamination and oxide film removal, however, at the present time it does not equal the 0.4 M CrSO_4 --0.5 M H_2SO_4 solution for several reasons. These are: (1) plutonium removal, (2) static corrosion rates, (3) cost of raw materials, and (4) the introduction of phosphorous into a sulfate system, which may be detrimental.

5.0 FEED MATERIALS (O. C. Dean)

5.1 Metallex (C. P. Johnston)

Efforts to optimize washing and pressing techniques to produce sintered thorium having a minimum of atmosphere connected voids were continued. Two sets of 3 experiments were carried out in duplicate in which thorium quasi-amalgam previously treated with 3 N HCl and water were treated as follows: (1) methanol washing followed by vacuum drying, (2) methanol washing, (3) water washing. In one set of experiments the resulting quasi-amalgams were pressed into slugs at about 10 tsi under argon, then sintered in a vacuum retort. In the other set, the amalgams were pressed in the open at 1/2 tsi, then vacuum retorted.

~~CONFIDENTIAL~~

DECLASSIFIED

The apparent density of the resulting sinters were all in relatively close agreement, 11.5 to 11.58. Bulk densities varied from 6.29 to 9.94, with the higher values found in the group pressed under argon. Atmosphere-connected voidage percentages ranged from 26.43 to 42.98 and appeared to be higher in experiments where pressing was carried out in the open. However, the difference in pressing pressure in the two series was quite large. This variable will be eliminated in another experiment series. Previous work by the Metallurgy Division has indicated that pressing pressure had little effect on the bulk density of sintered thorium.

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

6.1 Hydrochlorination (J. E. Savolainen)

6.1.1 Temperature on Hydrochlorination Rates

The hydrochlorination rate of an alloy, 97.89% U--2.11% Zr, is a function of the temperature as is shown in the following table:

<u>Temperature (°C)</u>	<u>Rate (mg/cm²·min)</u>
300	0.172
310-320	0.326
350	0.545
370	0.835

These rates were determined in a horizontal tube laboratory hydrochlorinator. The HCl flow rate was maintained sufficiently high so that an excess of HCl was present at all times. A single, small size piece of the alloy specimen was used to prevent excessive heating during hydrochlorination. No increase in the temperature was observed with the thermocouple adjacent to the alloy specimen when the hydrochlorination started.

The results show that the hydrochlorination rate can be controllably increased by increasing the temperature.

~~CONFIDENTIAL~~

- 9 -

6.1.2 Effect of Alloy Composition on Hydrochlorination Rates

The presence of low concentrations of silicon does not materially change the hydrochlorination rate of uranium metal. At 330°C, the observed hydrochlorination rate of uranium was 0.14 mg/cm²·min. At this same temperature, a 1% Si alloy reacted at 0.1 mg/cm²·min and a 2% Si alloy at 0.18 mg/cm²·min.

6.2 Dissolution of 2% Si-U Alloy in HNO₃ (A. H. Kibbey)

A 6 g sample of 2% Si-U alloy was completely dissolved in boiling 8 M HNO₃ under reflux. The insoluble silica residue which was removed and washed by centrifugation was found to contain 0.011% of the total uranium present.

6.3 Dissolution of Sodium Bonded Stainless Steel Fuel in Aqua Regia (A. H. Kibbey)

An APDA fuel element of stainless steel clad, sintered stainless steel core bonded with Na metal, was dissolved in excess 2 M HCl--5 M HNO₃ at 60-80°C. Dissolution was rapid, i.e., the 17.3 g sample dissolved completely in less than 24 min. The cladding was penetrated in approximately 1 min, after which time a series of minor explosions accompanied by brilliant flashes occurred as the Na was exposed to the aqueous solution. The dissolver solution was orange-brown rather than green, indicating that the dissolved chromium was being oxidized to the hexavalent state. The color obtained in previous similar runs indicated the presence of trivalent chromium. The reaction behavior is not considered to be so violent as to prohibit processing of this type of Na bonded stainless steel fuel element by this method.

6.4 Dejacketing of Zirconium Clad Mo-U Alloy (A. H. Kibbey)

The processing of zirconium clad 10% Mo-U alloy (APDA fuel) by dejacketing with a 900% excess of boiling 14 M H₂SO₄ followed by core

~~CONFIDENTIAL~~

DECLASSIFIED

~~CONFIDENTIAL~~

- 10 -

dissolution in a stoichiometric amount of 8 M HNO_3 was tested on laboratory scale. Results showed that the grey insoluble residue contained approximately $1/2$ and $1/4$, respectively, of the Mo and Zr present, but only 0.014% the total uranium. On the basis of these data, the processing of this type of fuel element by this method appears feasible.

7.0 FLUOROX
(R. G. Wymer)

7.1 Carbon Removal from UF_4 -C Pellets (L. M. Ferris)

When UO_3 is reduced and hydrofluorinated to UF_4 with starch and HF gas, respectively, there is always some residual carbon in the UF_4 . Since hydrogen is unreactive toward UF_4 at temperatures below $\sim 950^\circ\text{C}$, it was tried as a carbon removal agent at 475°C using a Ni boat and tube. The fact that no carbon was removed by this treatment shows that the Ni boat and tube did not act as the catalyst needed for the formation of methane. By utilizing nascent hydrogen from cracked NH_3 it may be possible to avoid the use of a catalyst.

7.2 UF_4 Surface Area Measurements (L. M. Ferris)

It has been found that the specific surface area of UO_2F_2 is much greater than that of UF_4 . Since pure UF_4 was not available, 98% UF_4 (2% UO_2F_2) was oxidized for an hour at various temperatures to obtain UF_4 - UO_2F_2 mixtures of known composition. It was hoped that the specific surface area of pure UF_4 at the various temperatures could then be obtained by extrapolation of the surface area data for UF_4 - UO_2F_2 mixtures. However, the data obtained were inconsistent and non-reproducible. Variations in UF_4 sintering rates, caused by packing the fine powder into a boat differently each time, probably account for most of the inconsistencies found. The 98% UF_4 (2% UO_2F_2) used in this study will

~~CONFIDENTIAL~~

DECLASSIFIED

~~CONFIDENTIAL~~

- 11 -

be purified by leaching the UO_2F_2 with H_2O . Surface areas as functions of time and temperature will then be evaluated for the purified UF_4 .

8.0 EXCER
(I. R. Higgins)

About 1-1/2 lbs of UF_4 have been produced at a tap density of 3.1 from synthetic ore leach in the 2-in. continuous contactor with one use of 5 M NaCl . Fixed bed cation exchange was used to remove Na and 2 M H_2SO_4 was added to the UO_2F_2 feed before electrolysis. The UF_4 was filtered on paper and dehydrated in a Mg tube. The specific surface area of the product was $1.1 \text{ m}^2/\text{g}$. The dehydration was not complete, 1.6% H_2O remained, and will be repeated. The sulfate content was 0.41% so the product will be rewashed. The boron content was 48 ppm or 5 times greater than in the original feed, which is difficult to understand because a DF of 1.6×10^4 was previously demonstrated across cation exchange and electrolysis. All other contaminants were within specification (see the following table).

Product Contaminants

Na-48 ppm	Cu-1.2
Ca-130	Ni-2.1
Fe-3.9	Cr- < 0.25
Al-30	V- < 5
Mg-6.8	Mn- < 0.25
Hg- < 13	Si-0.5
Pb-60	

~~CONFIDENTIAL~~

DECLASSIFIED

~~CONFIDENTIAL~~

- 12 -

9.0 FUSED SALT DISSOLUTION
(R. G. Wymer)

Ni corrosion specimens placed in the HF pump dissolver and exposed to flowing HF gas in $\text{NaF} \cdot \text{ZrF}_4$ at 600°C showed no detectable weight loss after 3-1/2 hr in two separate experiments. However, approximately 0.024 mole of non-condensable gas, presumably hydrogen, was generated indicating that the nickel dissolver and HF pump collectively lost ~ 1.4 g.

If high zirconium content fuel elements are to be dissolved in $\text{NaF} \cdot \text{ZrF}_4$ melts, it is of interest to know the effect of melt composition on dissolution rate at fixed temperature and HF flow rate. Rates of dissolution of 0.8 to $1.0 \text{ mg/min} \cdot \text{cm}^2$ were found for STR specimens in $\text{NaF}/\text{ZrF}_4 = 40/60$ melts at 600°C at a HF flow rate of 56 mg/min. These rates are to be compared with the rates of $4\text{--}5 \text{ mg/min} \cdot \text{cm}^2$ found when 1 to 1 melts are used, and with the still higher rates of $7\text{--}9 \text{ mg/min} \cdot \text{cm}^2$ found when $65/35 = \text{Na}/\text{ZrF}_4$ melts were used. At 600°C melts having a $40/60 = \text{NaF}/\text{ZrF}_4$ mole ratio are approximately saturated in ZrF_4 , and those having a mole ratio of $65/35 = \text{NaF}/\text{ZrF}_4$ are approximately saturated in NaF (see the phase diagram ORNL-LR-Dwg. 1201).

R. E. Blanco
R. E. Blanco

D. E. Ferguson
D. E. Ferguson

REB:DEF:igl

~~CONFIDENTIAL~~

DECLASSIFIED