OAK RIDGE NATIONAL LABORATORY LIBRARIES
3 4456 0549121 4

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

ORNL-TM-533

COPY NO. - 16

DATE - 4/1/63

CHEMICAL TECHNOLOGY DIVISION
MONTHLY REPORT FOR MARCH 1963

F. L. Culler, Jr.

ABSTRACT

Process development studies are reported on Power Reactor Fuel Processing (Shear-Leach Process Development, Processing Studies on Breeder Reactor Fuels, Uranium Dicarbide Metallographic Studies, Thorium Carbide Hydrolysis Studies, Chlorination Studies on UC_2-ThC_2-Graphite Fuels, Hydrochlorination Studies on U-Al Alloy Fuel, Corrosion Studies, Protactinium Adsorption Studies, Stripping of Uranium from 2.5% di-sec-Butylphenyl Phosphonate (DSBPP) in Diethylbenzene, Solvent Extraction Studies on UC Fuel Solutions, Fluoride Volatility Processing: Aluminum Alloy Flowsheet Development, Fluoride Volatility Processing: Dissolution and Fluorination in a Single Vessel, Fluoride Volatility Processing: Corrosion, and Fluoride Volatility Pilot Plant) and Chemistry Research (Chemical Engineering Research: Stacked Clone Contactor, Solvent Extraction Research, Process Chemistry of Uranium and Thorium, Volatility Studies, Ion Exchange Studies, Mechanisms of Separations Processes, and Chemical Applications of Nuclear Explosions).

NOTICE

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. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

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, expressed 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, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

CONTENTS

	Page
Power Reactor Fuel Processing	4
Shear-Leach Process Development	4
Processing Studies on Breeder Reactor Fuels	4
Uranium Dicarbide Metallographic Studies	4
Thorium Carbide Hydrolysis Studies	5
Chlorination Studies on UC_2-ThC_2-Graphite Fuels	6
Hydrochlorination Studies on U-Al Alloy Fuel	7
Corrosion Studies	9
Protactinium Adsorption Studies	9
Stripping of Uranium from 2.5% di-sec-Butylphenyl Phosphonate (DSBPP) in Diethylbenzene	10
Solvent Extraction Studies on UC Fuel Solutions	10
Fluoride Volatility Processing: Aluminum Alloy Flowsheet Development	12
Fluoride Volatility Processing: Retention of TeF_6	12
Fluoride Volatility Processing: Dissolution and Fluorination in a Single Vessel	13
Fluoride Volatility Processing: Corrosion	14
Fluoride Volatility Pilot Plant	15
Chemistry Research	17
Chemical Engineering Research: Stacked Clone Contactor	17
Solvent Extraction Research	17
Process Chemistry of Uranium and Thorium	19
Volatility Studies	19
Ion Exchange Studies	20
Mechanisms of Separations Processes	21
Chemical Applications of Nuclear Explosions	23

OAK RIDGE NATIONAL LABORATORY LIBRARIES

3 4456 0549121 4

POWER REACTOR FUEL PROCESSING

Shear-Leach Process Development. -- Bench-scale leaching tests on sheared ThO_2-UO_2 fuel were continued. Leaching of 1/2-in.-long sheared lengths of stainless-steel-clad ThO_2-UO_2 in a 4-in.-diam cylindircal dissolver resulted in the dissolution of 85% of the ThO_2-UO_2 in 2 hr in recirculating 12 M HNO_3--0.10 M Al--0.04 M NaF. The high dissolution rate demonstrated the effectiveness of an air-operated, adjustable draft tube in keeping the ThO_2-UO_2 fines in suspension. In comparison, two subsequent dissolution runs reached 85% dissolution in about 5 hr, apparently because of the poorer suspension produced by a fixed draft tube. Suspension of ThO_2-UO_2 fines during dissolution remains a major problem.

Processing Studies on Breeder Reactor Fuels. -- Studies on the kinetics of UO_2 pellet dissolution were continued. The instantaneous dissolution rate of UO_2 pellets having the same density (10.3 g/cm^3) in 14 M HNO_3 varied, depending upon the manufacturer; however, the times for complete dissolution of all pellets 1 cm long by 1 cm in diameter were about the same. The variation in apparent surface area during the dissolution compensated for the difference in initial rate (15 to 330 mg cm^{-2} min^{-1}), and the time for 90% dissolution varied only from 60 to 83 min.

Uranium Dicarbide Metallographic Studies. -- Heating of $UC_{2.00}$ or $UC_{1.91}$ (both with a combined-C/U ratio of 1.86) for 60 hr at 1450°C had no effect on the combined-C/U atom ratio, x-ray powder pattern, or amounts of gaseous hydrocarbons produced upon hydrolysis. The as-cast $UO_{2.00}$ was a two-phase mixture of $UC_{1.86}$ and graphite, which appeared as rod-shaped

areas in the photomicrographs. After heating, small platelets of a third phase were visible at 1000X. Similarly, as-cast $UC_{1.91}$, which appeared to be nearly single phase, contained the same small platelets after heating. These platelets have been observed in all dicarbide specimens after heat treating at temperatures between 1260 and 2000°C. There was no indication of any thermal decomposition of $UC_{1.86}$ to U_2C_3 and free carbon at temperatures below 1500°C, as reported by Battelle Memorial Institute.

Thorium Carbide Hydrolysis Studies. -- The maximum amount of carbon that could be combined with thorium by arc melting (using graphite electrodes) was 9.2 wt %, which corresponds to the composition $ThC_{1.95}$. Therefore, thorium dicarbide, like uranium dicarbide, is carbon deficient, although the thorium compound is much closer to the idealized MC_2 formula than uranium dicarbide is -- $UC_{1.85}$.

Reaction of thorium dicarbide samples (total-C/Th atom ratios of 1.95 and 2.14 and a combined-C/Th ratio of 1.95 in both cases) in water at 80°C yielded 49 ml (STP) of gas per gram of carbide. The evolved gas consisted of 30 vol % hydrogen, 3% methane, 32% ethane, 5% C_3-to-C_8 alkanes, 12% alkenes, 14% alkynes, and 2% unidentified unsaturates. This gas accounted for 50% of the combined carbon; an additional 12% was found as a water-insoluble, ether-soluble wax. The remaining 35% of the carbon could not be accounted for and presumably was soluble in the aqueous phase, which had a strong organic odor.

The thorium dicarbide hydrolysis products were in general similar to those from uranium dicarbide. The amounts of the various alkanes and alkenes produced in the hydrolysis of $ThC_{1.95}$ were nearly identical with those obtained by extrapolating the hydrolysis data on as-cast uranium

carbides to a hypothetical composition of $UC_{1.95}$. In addition, thorium dicarbide yielded significant quantities of alkynes, which accounted for 14% of the combined carbon and were principally acetylene and butyne-1. The alkyne content of the off-gas from $UC_{1.85}$ hydrolysis was only 1%, and no acetylene was observed. This accounts for the fact that the total carbon in the gas phase was 50% for $ThC_{1.95}$ vs 35% for hypothetical $UC_{1.95}$. Thorium dicarbide yielded less wax, 12% vs 25% for uranium dicarbide, and about the same amount of soluble organic compounds unaccounted for.

Thorium dicarbide, like uranium dicarbide, contains C_2 units in the crystal lattice, which yield predominantly C_2- or multiples of C_2-compounds upon hydrolysis. Hydrolysis of $ThC_{1.95}$, which approaches the idealized MC_2 formula, produced only 1% methane, in keeping with the hypothesis that methane is the hydrolysis product only of single C units in the crystal lattice and that the C-C bonds in C_2 units are not broken during hydrolysis. The thorium dicarbide structure is not exactly the same as that of uranium dicarbide, so some variation in hydrolysis products might be expected.

Chlorination Studies on UC_2-ThC_2-Graphite Fuels. -- Three 10-g samples of UC_2-ThC_2-graphite fuel containing 1.5% uranium and 7% thorium were burned in oxygen at 800°C in 2.5 to 3.5 hr. The product ash was then chlorinated in 2 hr with 15% CCl_4--Cl_2 at 500 and 550°C for two of the samples, and in phosgene at 500°C for the third sample. Complete chlorination was achieved, and the unvolatilized products were completely soluble in water in all three tests. The respective amounts of uranium volatilized from the residues during chlorination were: 74, 84, and 64%

of the total present. The volatilized uranium chlorides were collected on the cool exit of the reaction tube.

These experiments indicate that it is possible to process this type of fuel in a nickel vessel to yield an aqueous solution of the product, containing both the uranium and thorium. Quantitative separation of uranium and thorium may be possible by using higher temperatures to completely volatilize the uranium as uranium chloride, but ceramic vessels would have to be used because metal vessels would corrode too rapidly at the temperatures required.

Hydrochlorination Studies on U-Al Alloy Fuel. -- The maximum steady-state temperature during hydrochlorination of an MTR fuel element, as calculated with the GHTR heat transfer code on the IBM 7090 computer, was found to decrease from 1073°C at a hydrochlorination rate of 12 mils/hr to 549°C at a rate of 6 mils/hr. At the average rate of 6 mils/hr, the 60-mil-thick inside plates and the 180-mil side plates could be completely hydrochlorinated in 5 and 15 hr, respectively. The additional small contribution to heat removal by the heat capacity and convection of gases present was not considered. These results indicate it will be possible to hydrochlorinate MTR fuel elements at rather low rates without exceeding the melting temperature of the fuel, 650°C.

An experiment showed that the volatile-uranium loss during hydrochlorination of an about 8% U--Al alloy could be held to 0.5%. The experiment was designed only to investigate the beneficial effect of using carbon monoxide as a carrier gas. Mixed chlorides of uranium and aluminum were prepared by chlorinating and volatilizing the U-Al alloy and then condensing and collecting the volatilized chlorides at room temperature.

Three runs were then made by passing argon at 300°C, carbon monoxide at 300°C, and carbon monoxide at 200°C over separate samples of the mixed uranium and aluminum chlorides in order to selectively volatilize the aluminum chloride. The percentages of uranium lost by volatilization with the aluminum were 18.3, 8.3, and 0.5, respectively. Slightly volatile fractions collected in the hot zone contained 59.7, 2.7, and 97.9% of the uranium, respectively. This fraction also contained from 2 to 4% of the aluminum in all three cases. An additional 22.0, 88.9, and 1.6% of the uranium, respectively, was found in the nonvolatile fraction from each run, along with 3 to 6% of the aluminum.

It is apparent that the use of the higher temperature of 300°C with argon, and particularly with carbon monoxide, helped keep uranium in the nonvolatile fraction, while the use of the lower temperature of 200°C with carbon monoxide caused the volatilized uranium to redeposit almost quantitatively within the hot zone, thereby greatly decreasing the amount of uranium lost by volatilization with the aluminum. Therefore, a separation procedure is suggested, based on the selective condensation of uranium chloride from a vapor of the mixed chlorides in a chamber, the entrance and exit ends of which are heated to about 300 to 200°C, respectively, using carbon monoxide as a carrier gas.

The beneficial effect of carbon monoxide in these experiments can be explained by its ability to reduce volatile uranium chlorides in the gas phase to lower-valent, nonvolatile compounds. The loss of uranium by volatilization is a serious problem in the hydrochlorination of U-Al alloys because the $AlCl_3$ chlorination product is capable of oxidizing much of the normally expected uranium chloride (UCl_3) to higher-valent, volatile chlorides.

Corrosion Studies. -- Two sets of corrosion experiments were made in order to evaluate various materials of construction for Chloride Volatility Processes. Haynes 25, Nichrome V, INOR-8, nickel, and type 304L stainless steel corroded at maximum rates of 0.02, 0.08, 0.01, 0.05, and 0.12 mil/month, respectively, for 264-hr exposures in hexachloropropene or its vapors at 185 to 190°C. Rates for niobium and tantalum for similar exposures of 168 hr were 0.95 and 0.05 mil/month, respectively. In oxidation-chlorination cyclic tests consisting of 5 hr in O_2 at 800°C followed by 5 hr in Cl_2-CCl_4 at 500°C, rates for five cycles of exposure with INOR-8, Nichrome V, and "A" nickel were 24, 7, and 754 mils/month, respectively. Specimens exposed during cycling in the development of the process on a laboratory scale did not show such high rates.

Protactinium Adsorption Studies. -- Studies on the adsorption of protactinium on unfired Vycor were continued. Protactinium-233 was decontaminated from uranium by a factor of 1.59×10^4, using a column 10 mm in diameter and 8.6 cm long, containing 5 g of 60- to 80-mesh unfired Vycor. The feed solution contained uranium, 11.2 mg/ml; thorium, 9 mg/ml; fluoride, 0.04 M; aluminum, 0.1 M. It was 10 M in HNO_3, and the Pa^{233} concentration was equivalent to 2.04×10^6 counts min^{-1} ml^{-1}. The solution flow rate was 0.64 ml min^{-1} cm^{-2}. After washing the loaded column with 28 ml of 10 M HNO_3, about 80% of the protactinium was recovered by eluting with 18 ml of 0.5 M oxalic acid. The uranium in the combined raffinate and wash was decontaminated from the protactinium by a factor of 44.

The corrosion of the unfired Vycor by the fluoride in the feed solutions was decreased by more than a factor of 50 by the presence of 2.5

moles of aluminum per mole of fluoride ion. Solutions 0.05 M in HF and 11 M in HNO_3, with and without 0.12 M Al, were passed through columns 4 mm in diameter and 9 cm long containing 1 g of 60- to 80-mesh unfired Vycor at a flow rate of about 1 ml min^{-1} cm^{-2}. After about 200 ml had passed through the columns, the emerging raffinate from the aluminum feed solution contained silicon to extent of 0.006 mg/ml, whereas the solution without the aluminum contained 0.32 mg/ml.

Stripping of Uranium from 2.5% di-sec-Butylphenyl Phosphonate (DSBPP) in Diethylbenzene. -- The discrepancy between laboratory, Unit Operations, and pilot-plant data of the stripping of uranium from 2.5% DSBPP in DEB is apparently due to degradation products in the solvent. Used solvent from the pilot plant was equilibrated with a feed solution containing U^{233} and then exhaustively stripped with one-quarter volume of water. The stripping coefficient decreased from about 200 with the first contact to a constant 0.5 after the fifth contact. This indicated that about 1% of the uranium (5×10^4 counts min^{-1} ml^{-1}) was strongly complexed by the solvent, probably due to the presence of organic degradation products.

Solvent Extraction Studies on UC Fuel Solutions. -- The UC in sheared, stainless-steel-clad uranium monocarbide [Consumer's Public Power District reactor (CPPD), core 2] reactor fuel may be converted to uranyl nitrate-nitric acid solution for Purex solvent extraction either by hydrolysis with water at 80 to 100°C to yield hydrous UO_2, followed by dissolution in nitric acid, or by direct dissolution with nitric acid. Investigation of the first alternative head-end procedure has progressed to the stage where a head-end chemical flowsheet coupled to a conventional Purex flowsheet has been devised and is being cold-tested.

Hydrolysis of 30-g specimens of impure UC containing 5.1% C with water at an H_2O/UC mole ratio of 20, at 90°C for 4 hr, yielded a thick slurry of hydrous UO_2. Dissolution of the slurry in boiling 8 M HNO_3 for 2 hr yielded an orange-colored, raw feed solution that was 2 M in HNO_3, with a uranium concentration of 300 g/liter. This feed solution, in contrast to more dilute feeds prepared by dissolution in 4 M HNO_3, was free of waxy solids. The concentrated raw feed contained traces of soluble organic acids that resulted from hydrolysis of the dicarbide impurity in the fuel. Unless removed or destroyed, these compounds act as emulsifiers and strong complexing agents for uranium and cannot be tolerated in the Purex system.

The organic acids can be degraded by oxidation to organic compounds that do not affect solvent extraction. Digestion of the raw feed with either 0.02 M $KMnO_4$ or 0.05 M $Ce(NH_4)_2(NO_3)_6$ at 70° for 3 hr appears equally effective. After removal of the MnO_2 precipitate, the finished feed solution, when tested by exhaustive extraction with 30% tributyl phosphate in Adakane and exhaustive stripping with 0.01 M HNO_3, exhibited no unusual emulsification or interfacial crud. Uranium losses during extraction and stripping were negligible, being less than 0.01% in each step. Almost identical results were obtained when the feed was treated with ceric ion. The latter treatment may be preferred, since it does not require a feed-clarification step.

Infrared spectroscopy indicated that oxidation of the organic acids yields largely aliphatic compounds that may be partially nitrated. The path of these organic end products through solvent extraction has not yet been determined, pending the development of a suitable analytical procedure.

Fluoride Volatility Processing: Aluminum Alloy Flowsheet Development. -- In continuing phase-equilibrium studies, liquidus isotherms in the system $LiF-KF-AlF_3$ at temperatures below 800°C were tentatively established. The 600°C isotherm includes $LiF-KF-AlF_3$ compositions containing greater than and less than 25 mole % AlF_3. The minimum temperature in the quasi-binary system, $3LiF \cdot AlF_3-3KF \cdot AlF_3$, was 645°C at 25.5 mole % $3LiF \cdot AlF_3$. In an attempt to obtain lower-melting solvents for AlF_3, additional components, as alkaline earth fluorides, were added to $3LiF \cdot AlF_3-3KF \cdot AlF_3$ mixtures. Combinations of the alkaline earth fluorides, MgF_2, CaF_2, SrF_2, and BaF_2, whose optimal proportions have not yet been determined, lowered the solidus temperature for $3LiF \cdot AlF_3$-$3KF \cdot AlF_3$ mixtures by as much as 70°C.

Preliminary laboratory-scale tests designed to measure aluminum dissolution rates at 600°C in 50-50, 60-40, and 65-35 mole % LiF-KF were unsuccessful because of solids formation upon introduction of HF, and subsequent foaming. The same effects were found in sparging 46.5-11.5-42.0 mole % LiF-NaF-KF (Flinak), thus tending to confirm the hypothesis that KF forms such a stable complex with HF that a phase transition is produced.

Fluoride Volatility Processing: Retention of TeF_6. -- Gas-liquid absorption tests in packed columns 1-in. diam and 20 in. long were made in order to examine the behavior of the TeF_6 in the Volatility Pilot Plant fluorine-disposal spray tower. During the four tests, about 10 mole % TeF_6 in 100 ml/min of fluorine was passed through the columns countercurrent to 10% aqueous KOH. In two runs at ambient temperature, the absorption efficiencies appeared to be greater than 20%, while at

a column temperature of 70°C, the efficiencies were greater than 50%. However, these efficiency values are only approximate since there was considerable uncertainty in the amount of TeF_6 introduced in each test. More exact tests are planned.

Fluoride Volatility Processing: Dissolution and Fluorination in a Single Vessel. -- Recent engineering-scale studies of the hydrofluorination and subsequent fluorination of Zr--6% U alloy fuel elements (simulated) in the same INOR-8 vessel showed a range of specific dissolution rates comparable to that found in previous studies, and no unusual fluorination or corrosion results. Six dissolution-fluorination sequences were made in 35-35-30 mole % $NaF-LiF-ZrF_4$ at 550°C with HF and F_2. Two additional fluorinations only were made after the completion of the six cycles. Specific dissolution rates varied between 0.8 and 1.55 mg cm^{-2} min^{-1}, while the fluorination half-times varied between 40 and 135 min. Some dissolution off-gas difficulties were experienced throughout the series, and the $HF-F_2$ inlet line failed during the startup of the fourth dissolution.

One INOR-8 and two Alloy 79-4 corrosion specimens were suspended in the salt during five of the dissolution-fluorination cycles, the two additional fluorinations, and an aqueous-ammonium-oxalate-solution cleaning step. The 24-in.-long rods were suspended so that they penetrated the vapor-liquid interface. The maximum penetration by micrometer measurements for the INOR-8 was 11 mils in the interface region, while for Alloy 79-4 it was 5 mils in the liquid region. The corrosion rods were in contact with molten salt for about 550 hr, of which time 64 hr were with HF present and 32 with F_2 present. Based on fluorine contact time, the corrosion rates for the rods were 0.33 mil/hr and 0.16 mil/hr

for INOR-8 and Alloy 79-4, respectively. Vidigage measurements of the INOR-8 vessel showed that maximum penetrations of 25 and 20 mils occurred in the vapor region and interface region, respectively.

Fluoride Volatility Processing: Corrosion. -- The dissolution of Zircaloy-2 with HF in 36.9-27.0-9.1-27.0 mole % $NaF-LiF-BeF_2-ZrF_4$ was found to be only mildly corrosive at 500°C when studied in the laboratory at Battelle Memorial Institute. Specimens of INOR-8, HyMu 80, L-Nickel, Alloy 2 (10-5-85 wt % Mo-Fe-Ni), and Ni-5 Fe were tested. INOR-8, HyMu 80, and L-Nickel specimens with welds in which the respective base metals were used as a filler metal were tested, as were specimens of L-Nickel welded with INCO-41 and -61. The maximum corrosion rate by weight loss was 0.57 mil/month of HF exposure for L-Nickel welded with INCO-61. The rates for HyMu 80 and INOR-8 were similar, with a maximum of 0.27 mil/month of HF time. Significant intergranular attack was observed only on unwelded and self-welded L-Nickel and the Ni-5 Fe specimens. Difficulty was experienced in obtaining meaningful Zircaloy-2 dissolution rates over the entire run, but at 20 and 96 hr, rates were apparently only 0.4 and 0.2 mil/hr, respectively, based on H_2 evolution.

Memorandum BMI-X-218 (Feb. 15, 1963) presents the results of the examination of specimens removed from the Volatility Pilot Plant fluorinator after aqueous decontamination, and results of the simulated decontamination regime (ORNL-3410, p 9). The maximum base-metal corrosion rates for the specimens removed from the L-Nickel fluorinator were 0.38 mil per hour of fluorine exposure, including aqueous decontamination losses, and 0.26 mil per hour of fluorine time, excluding aqueous decontamination losses. Total molten-salt exposure time for the fluorinator was 1920 hr; fluorine exposure time was 57.5 hr.

BMI-X-218 also presented results of the metallographic examination of the corrosion specimens exposed in the Volatility Pilot Plant fluorinator during runs TU-11, -12, R-1 to -6, T-11, and the aqueous decontamination program. Salt exposure time was 625 hr at 520°C maximum, including 20.8 hr of fluorine. The maximum total corrosion rates were 0.32, 1.83, 0.99, 1.31, 0.36, and 2.62 mils per hour of fluorine time for L-Nickel, Ni-1 Al, Ni-5 Mo, INOR-1, INOR-8, and HyMu 80, respectively. The high corrosion rate for HyMu 80 is attributed to attack by the $Al(NO_3)_3$-HNO_3 solution during the aqueous decontamination program.

Fluoride Volatility Pilot Plant. -- After completion of fluorine leak testing of the Volatility Pilot Plant, inert gas was passed through the plant at temperature, using normal flow patterns. A salt-transfer test was then made. In spite of the aqueous decontamination program that had been carried out, radiation intensities at the waste-salt can ranged from 50 to 400 mr/hr.

Two complete runs with unirradiated fuel were made. In general, the runs were successful, but there were difficulties in melting the salt in transfer lines in both runs. Modifications should correct the difficulties. At least one more cold run will be required prior to hot operations.

In both runs, the standard fluorination procedure (101 min at 6 slm followed by 19 min at 13 slm) was followed. In run TU-14, this procedure reduced the uranium content to an acceptable value (less than 10 ppm); however, in TU-13 only 99% of the uranium was volatilized, and an additional fluorination period was required. The reason for the incomplete fluorination during the first run is not known. In both runs, the movable absorber operated quite smoothly, and a 25% bed discharge at the end of each run added no uranium to the waste salt.

A molybdenum-stripping operation at 150°C was included in the UF_6 absorption procedure. In TU-13, the anticipated amount of molybdenum was removed, but the product was still contaminated with it. The source of this additional molybdenum has not been determined, and analyses from the TU-14 product are not yet available.

The product from both runs was contaminated with HF. An HF flashing operation was included in the product-handling procedure but apparently was inadequate. The source of the HF (several hundred grams in each run) has not been determined.

CHEMISTRY RESEARCH

Chemical Engineering Research: Stacked Clone Contactor. -- A new design series of contactor, designated the Mark X series, was built and tested in its first conformations with the system: 1 M $NaNO_3$, $UO_2(NO_3)_2$, 18% tributyl phosphate in Amsco. The contactor exhibited flooding throughputs over 4.5 liters/min at stage efficiencies of 60 to 65%, giving a "performance factor" (throughput x efficiency) of 2.7 to 2.9. This compares with a factor of 2.3 for the best performance of previous contactors (Mark VI). The new series has features suggested by previous tests: an underflow skirt, a mixing chamber between the underflow port of one stage and the vortex finder of the stage below, and a baffled passage between the mixing chamber and the pump suction plenum designed to promote radially symmetrical flow.

Solvent Extraction Research. -- In comparative tests with several solvents Am(III) was usually extracted preferentially to Am(VI) from nitrate solutions. Single-stage separation factors attained from various systems included: greater than 10,000 with di(2-ethylhexyl)phosphoric acid from nitric acid, 100 with tri-n-octylphosphine oxide from sodium nitrate, and 30 with tributyl phosphate from lithium nitrate. In extractions by tertiary amines, the differences were smaller and sometimes were in the opposite direction. These data indicate possible applications to separation of americium from curium, which cannot be oxidized in solution and which usually extracts slightly better than Am(III).

Continued studies of strontium extraction from sodium nitrate solutions by di(2-ethylhexyl)phosphoric acid ($[HA]_2$) and its sodium salt (NaA)

in benzene confirmed the previously suggested reaction: $Sr^{2+} + 3[HA]_2 \rightleftharpoons SrA_2 \cdot 4HA + 2H^+$ (ORNL-3331), and also the corresponding reaction $Na^+ + 2[HA]_2 \rightleftharpoons NaA \cdot 3HA + H^+$, when the extractant is preponderantly in the acid form, $[HA]_2$. When the extractant contains significant amounts of the sodium salt, the generalized equation, $Sr^{2+} + (n/y)\ [aHA \cdot bNaA]_y \rightleftharpoons SrA_2 \cdot (n-2)(\alpha HA \cdot \beta NaA) + iH^+ + jNa^+$, $a+b = 1$, $\alpha+\beta = 1$, $i+j = 2$, has proved to be a suitable model at least up to 50% salt form. Experimental evaluation of i from H^+ concentration dependence, n/y from extractant concentration dependence, and y from vapor pressure measurements (ORNL-3368) leads to calculated values of n in the range 4 to 6, indicating that the extracted strontium is in the form of $SrA_2 \cdot 4HA$ or analogous adducts throughout this region.

Triphenylmethane was used as a reference standard in relative osmotic measurements of organic solutions by the isopiestic vapor-balancing technique (ORNL-2166, -2578), although there was evidence of some deviation from ideality (ORNL-2845). Its activity coefficients in benzene solution have now been determined by the direct differential vapor-pressure technique (ORNL-3120), varying from 0.98 at 0.014 m to 0.74 at 0.33 m. Activity coefficients of azobenzene, another useful reference solute, were then determined in benzene solution by isopiestic balancing with the triphenylmethane, ranging from 0.96 at 0.0134 m to 0.67 at 0.346 m. Thus, both of these reference solutes are now available for absolute as well as relative isopiestic measurements.

The efficiency of a pulsed solvent extraction column at a high aqueous-to-solvent flow ratio (100:1) was tested with 30% tributyl phosphate to extract uranyl nitrate from 4 M $NaNO_3$ solution. The HETS

of a nozzle-plate cartridge (0.125-in. holes, 10% free area), operated with the organic phase continuous, was 6.3 ft at a pulse of 35 cpm and a 1-in. amplitude.

Process Chemistry of Uranium and Thorium. -- Beryllium has been recovered from ore sulfate leach liquors (pH about 2.5) by extracting with primary amines. Of the compounds tested, best results were obtained with 1-(3-ethylpentyl)-4-ethyloctylamine. The beryllium extraction coefficients increased with increase in sulfate concentration in the range 0.5 to 2 M and were higher for 10-min than for 60-min contact times.

Results of preliminary tests show possibilities for applying solvent extraction with amine reagents to the recovery and purification of phosphoric acid from commerical phosphoric acid. Tertiary amines with a moderate degree of steric hindrance, for example, benzyldilaurylamine and 2-ethylhexyldilaurylamine, showed the best balance between phosphoric acid extraction power and ease of stripping with water.

Volatility Studies. -- A method for preparing granular LiF with a high specific surface area has been developed for use in PuF_6 studies. It consists of fusing Li_2CO_3, solidifying, and then slowly fluorinating with elemental F_2 at ambient temperature. A surface area of about 40 m^2/g was obtained with the material, and it had sufficient granular strength for use in adsorption beds. Granular LiF was obtained from ORGDP with an area of only 1.6 m^2/g for comparative tests in the PuF_6 work. It was prepared from analytical grade powder by a wet compaction and drying method. The fusion-fluorination method may be useful in the preparation of other sorbent fluorides of high surface area.

The first test with a stirred reactor on the volatilization of PuF_6 from fused $LiF-NaF-ZrF_4$ salt was unfavorable, with the volatilization rate being approximately the same as in previous static tests. However, this test lasted less than an hour, and it was evident that further improvements in the design of both the stirrer and the reactor were desirable.

Ion Exchange Studies. -- Citric acid was evaluated as a complexing agent for aluminum, iron (Fe^{3+}) and chromium (Cr^{3+}) at a pH of 2.5 -- a higher acidity than is routinely considered. Bulk quantities of these trivalent cations interfered with the direct use of cation exchange for recovering useful fission products from radioactive waste solutions. For the specific case of Purex IWW waste, the capacity for strontium was less than one resin volume of solution because the molar concentration of iron in the waste was more than 100 times that of the strontium. Previous studies with oxalic acid indicated that it complexed iron effectively and, correspondingly, increased the resin capacity for strontium three-fold. However, oxalates precipitated on the resin bed as the acidity of the local exchange zone was lowered to pH between 0 and 2 by the displacement of hydrogen ion with such sorbable cations as the rare earths and strontium.

Distribution coefficients were determined for rare earths (Ce^{3+}), strontium, and iron (Fe^{3+}) in the acid concentration range of 0.1 N--1.1 N, corresponding to waste Purex IWW waste dilutions of 5 to 40. Major cationic impurities were complexed by (1) adding citric acid in the ratio of 1.5 moles per mole of combined Fe^{3+}, Al^{3+}, and Cr^{3+}, (2) adjusting to pH 2.5 with concentrated ammonia, and (3) heating the solution to 90 to 100°C for 0.5 hr to ensure complete complexing of the

chromium ion. The resin used in the experiments, Dowex 50W X-8 (100 to 200 mesh), was equilibrated with a 0.5 M HNO_3--0.005 M ammonium citrate solution at pH 2.5 prior to its use.

Distribution coefficients for both strontium and rare earths increased as the acidity was lowered by dilution. Strontium values followed a second-power dependence, as predicted for a divalent cation, ranging from 10 to 800 as the acidity was lowered from 1.1 N to 0.1 N. Rare earth (Ce^{3+}) distribution coefficients varied from 3 to 2300 over the same acid concentration range, but did not follow the predicted third-power dependence for a trivalent cation. Ferric ion was very strongly complexed by the citrate ion even at a waste-dilution factor of 400 (0.014 N), while the distribution coefficient remained less than 0.3. Plotted experimental data indicated that at a reasonable dilution factor (20), more than three volumes of original Purex IWW could be processed per volume of resin before strontium breakthrough and that favorable separation of the various fission products from each other and from iron would occur, that is, K_d^{Sr}/K_d^{Fe} greater than 200, K_d^{Ce}/K_d^{Fe} greater than 600 and K_d^{Ce}/K_d^{Sr} greater than 3.

Mechanisms of Separations Processes. -- In continuation of studies of the thermodynamics of extraction of uranyl nitrate and nitric acid by tributyl phosphate, additional measurements of the partial pressures of water and acid over the three-component system H_2O-HNO_3-$UO_2(NO_3)_2$ were made. Acid concentrations ranged from 3 to 17 m, uranyl nitrate from 0 to 1.8 m (near saturation).

To obtain by calculation the activities of uranyl nitrate from the measured activities of water and nitric acid, it is necessary to integrate

the Gibbs-Duhem equation for this three-component system. It was found here that by appropriate choice of the paths of the integration that the integration can be performed exactly and that the final equation assumes a very simple form:

$$\frac{n_2}{n_1} \ln [a_2(n_2,n_3)/a_2(n_2,0)] + \frac{n_3}{n_1} \ln [a_3(n_2,n_3)/a_3(0,n_3)] = \ln \left\{[a_1(n_2,n_3)]/[a_1(n_2,0)a_1(0,n_3)]\right\} . \quad (1)$$

In this equation, subscripts 1,2, and 3 refer to H_2O, HNO_3 and $UO_2(NO_3)_2$, respectively; n_i is the number of moles of component i in the solution; $a_i(n_2,n_3)$ is the activity of component i in a solution containing n_2 moles of HNO_3 and n_3 moles of $UO_2(NO_3)_2$. A zero within parentheses indicates that a component is not in the solution; for example, $a_1(0,n_3)$ is the activity of water over H_2O-$UO_2(NO_3)_2$ solution.

Measurements of water vapor pressure over 26 solutions show that $[a_1(n_2,n_3)]/[a_1(n_2,0)\ a_1(0,n_3)]$ is 1.008, with a standard deviation of 0.034; that is, this term is unity, within experimental error. Thus, the term on the right of Eq. (1) is zero, and we can calculate the activities of uranyl nitrate in the three-component solutions from the measured activities $[a_2(n_2,n_3)]$ of nitric acid in the three-component solution and literature data on activities of nitric acid in the two-component solution H_2O-HNO_3 [i.e., $a_2(n_2,0)$] and activities of uranyl nitrate in the two-component solution H_2O-$UO_2(NO_3)_2$ [i.e., $a_3(0,n_3)$].

Experimental data show that the term: $n_2 \ln [a_2(n_2,n_3)/a_2(n_2,0)] = -n_3 \ln [a_3(n_2,n_3)/a_3(0,n_3)]$ is nearly (but not exactly) a linear function of m_3, the molality of $UO_2(NO_3)_2$ in the solution. They show that, to a first approximation, nitric acid does not change the activity of uranyl

nitrate (at constant uranyl nitrate molality), although uranyl nitrate increases the activity of nitric acid. These results may be summarized as follows:

$$\ln [a_2(n_2,n_3)/a_2(n_2,0)] \cong \frac{5(m_3)^x}{m_2} , \qquad (2)$$

where x may be nearly unity(but not identically unity).

Although further analysis of the data is necessary, the form of Eq. (2) shows that the three-component system H_2O-HNO_3-$UO_2(NO_3)_2$ does not follow the Harned rule for interaction of two solutes in water.

The integration of the Gibbs-Duhem equation was extended to aqueous solutions containing three solutes, and the procedure can readily be extended to even more complex solutions. It therefore appears probable that the present thermodynamic study can be easily extended to extraction of trace components (such as fission products, and perhaps studied one at a time) from H_2O-HNO_3-$UO_2(NO_3)_2$ solutions.

Chemical Applications of Nuclear Explosions. -- Water-leaching studies of a large composite sample of known particle-size distribution from the Gnome event showed that the water-soluble material is dissolved in 30 min or less. The percentages of water-insoluble residue remaining after leaching at room temperature were 8.8, 8.1, 7.1, 6.0, and 5.8 for water-to-sample-weight ratios of 2.8, 3.3, 4.2, 5.6, and 6.9, respectively. The quantity of insolubles was about 20% less in 30-min leach tests than in 24-hr leach tests for water-to-sample ratios less than 5.3, indicating that it is possible to supersaturate the solutions in short leach periods. Removal of activity by nitric acid leaching is independent of acid concentration above 1 N when excess acid is used. Acid consumption was 15 to 20 milliequivalents per gram of residue leached. Although ferric

hydroxide was shown to be an effective scavenger of Am, Cm, Pu, and Eu from leach solutions, at pH's above 6, the leach solutions contained too much ferric iron to give good decontamination factors. When all of the iron was precipitated, the ferric hydroxide retained about a third of the solution volume in its gel structure. Oxalate precipitation of Ce^{3+} carrier or of very small acounts of calcium quantitatively carried $Eu^{152-154}$ tracer from 1 N HNO_3 solutions saturated with $CaSO_4$ in which the ferric ion concentration was varied from 0.5 to 1.5 mg/ml. The pH of the solutions was adjusted to 1.0 to 1.5 with NaOH to cause precipitation. Cerous ion concentrations as low as 100 ppm, or calcium in this equivalent, were used to quantitatively carry the europium as oxalate.

INTERNAL DISTRIBUTION

1. R. E. Blanco
2. J. O. Blomeke
3. J. C. Bresee
4. K. B. Brown
5. F. R. Bruce
6. F. L. Culler
7. D. E. Ferguson
8. H. E. Goeller
9. A. T. Gresky
10. M. J. Skinner
11. E. G. Struxness
12. W. E. Unger
13. M. E. Whatley
14. H. B. Whetsel
15. R. G. Wymer

16-17. Central Research Library
18. Document Reference Section
19-31. Laboratory Records
32. Laboratory Records (RC)

EXTERNAL DISTRIBUTION

33. P. C. Aebersold, Washington AEC
34. B. Anderson, COO
35. E. L. Anderson, Washington AEC
36. W. Belter, Washington AEC
37. S. Bernstein, UCNC, Paducah
38. J. A. Buckham, ICPP
39. J. T. Cristy, HOO
40. A. Friedman, Washington AEC
41. R. R. Hayward, AI
42. S. Lawroski, ANL
43. J. A. Lieberman, Washington AEC
44-45. J. A. McBride, ICPP
46. B. Manowitz, BNL
47. J. W. Morris, SRP
48. H. Pearlman, AI
49. J. W. Pollock, IDO
50. W. H. Reas, HAPO
51. B. Schwartz, Washington AEC
52. J. M. Simmons, Washington AEC
53. C. M. Slansky, ICPP
54. C. E. Stevenson, IDO (ANL)
55. V. R. Thayer, du Pont, Wilmington
56. L. Topper, NYOO
57. A. F. Voigt, ISC
58. W. E. Winsche, BNL
59. L. L. Wyman, NBS
60-74. DTIE
75. Research and Development, ORO