



OAK RIDGE NATIONAL LABORATORY LIBRARIES



3 4456 0548524 9

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

UNION
CARBIDE

ORNL - TM - 126

COPY NO. - 18

DATE - 2/1/62

CHEMICAL TECHNOLOGY DIVISION
MONTHLY REPORT FOR JANUARY 1962

F. L. Culler, Jr.

ABSTRACT

Process development studies are reported on Power Reactor Fuel Processing, Fluoride Volatility Processing, Mechanisms of Separations Processes, Solvent Extraction Studies, and Chemical Applications of Nuclear Explosions.

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.

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.

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.

CHEMICAL TECHNOLOGY DIVISION
MONTHLY REPORT FOR JANUARY 1962
POWER REACTOR FUEL PROCESSING

Corrosion. Unwelded Corronel 230 exposed to boiling 20 M HNO_3 for 384 hr was corroded at rates of 7.3, 0.88, and 0.62 mils/mo in the vapor, interface, and solution phases, respectively. Vapor zone specimens appeared to have undergone intergranular attack. In boiling 10 M HNO_3 —0.5 M NaF —0.75 M $\text{Al}(\text{NO}_3)_3$, unwelded Corronel 230 was corroded at rates of 0.82, 0.78, and 0.81 mil/mo in vapor, interface, and solution, respectively, in 240 hr exposure. Corresponding rates for welded titanium-45A were 0.04, 0.20, and 0.34 mil/mo. Unwelded Corronel 230 was corroded at rates of 3.70, 12.3, and 25.2 mils/mo in 48 hr exposure to vapor, interface, and solution, respectively, of refluxing 1 M HF . These data will serve as a base line for corrosion tests in flowing HF - H_2O_2 solutions.

In 24 hr corrosion of Haynes 25 in chlorine increased from about 6 mils/mo at 500°C to 1290 mils/mo at 730°C; corresponding rates for Nichrome V were 2.4 and 650 mils/mo.

Darex Process. In further development work on countercurrent stripping of chloride from Darex dissolver solutions with N_2O_4 - NO_2 equilibrium mixtures at 45-55°C in a 2-in.-dia column 6 ft high packed with 1/4-in. Berl saddles, chloride was removed to < 350 ppm as compared to ~3000 ppm in a 3-ft-high column with 500-600% excess NO_2 . Extrapolation of the data indicates that chloride can probably be removed to < 350 ppm with 200% excess NO_2 in a column 12-24 ft high.

In 1-liter laboratory-scale runs with a batch dissolver and a continuous, titanium-ring-packed, chloride stripper column, Darex dissolution of APPR fuel yielded 1.7 wt % gelatinous precipitate, predominantly SiO_2 , which clung to vessel walls and readily plugged the stripper column. The addition of 0.01 to 0.04 M fluoboric acid to the dissolvent solubilized the silica when dissolution was to 24 g of stainless steel per liter. At higher fuel loadings, 24 to 60 g of stainless steel per liter, SiO_2 solubility decreased sharply even though the F/Si mole ratio was constant,



but as little as 0.01 M HBF_4 produced a granular, rapidly settling precipitate. About 87% of this material passed through the system; the remainder, which was held up in the stripper column, was easily washed out with hot dilute HNO_3 . About 11% of the fluoride appeared in the overhead condensate (0.015 M F) when the dissolvent contained 0.02 M HBF_4 .

Graphite and UC Fuel. Combustion of UO_2 -graphite fuels containing iron as an impurity produces an ash from which uranium cannot be completely leached with boiling nitric acid. The amount of uranium lost to the acid-insoluble residue decreased from 2 to 0.1% as the Fe/U mole ratio in the fuel decreased from 2.4 to 0.09.

Type GBF graphite reacted slowly with boiling 90% HNO_3 , only 60-70% being oxidized in 200-500 hr. The chief products were CO_2 and CO, although 3-6% of the carbon was converted to water-soluble organic acids, mainly (60-80%) mellitic acid. No evidence for nitration of the soluble organic products was found.

Specimens of $\text{UC}_{1.5}$, $\text{UC}_{1.6}$, and $\text{UC}_{1.7}$ that had not been heat-treated yielded less methane on hydrolysis than UC. Greater quantities of water-soluble organic species and about the same amounts of C_2 to C_8 hydrocarbons were also observed with increasing carbon concentration in the specimens.

Solvent Extraction Studies. In studies on Purex and Interim-23 type flowsheets for removing Th-228 and U-233 containing ~100 ppm of U-232, uranium was decontaminated from thorium by a factor of ~100 and met U-233 product specifications. In the tests synthetic feed solutions were extracted with (a) 30% TBP in Amsco and scrubbed with aluminum nitrate or ammonium nitrate containing fluoride, and (b) 2.5% TBP and scrubbed with either a static or countercurrent aluminum nitrate solution. Uranium holdup in the static scrub was, however, too high for practical application.

The soluble organic materials resulting from leaching of unirradiated UO_2 -graphite Pebble Bed Reactor fuel with 90% HNO_3 had no apparent deleterious effect on uranium extraction with TBP, decontamination, or stripping. Fission product had been added to the 90% HNO_3 dissolvent prior to the leaching. Excess acid was removed by evaporation, and the uranium was extracted with 5% TBP in Amsco and stripped with 0.01 N HNO_3 .

Uranium loss to the aqueous raffinate was 0.3%, and to the stripped solvent, < 0.01%. The gross decontamination factor was 6000.

A column 27 cm long by 8 mm dia containing 80-100 mesh unfired Vycor glass removed 96.6% of the protactinium and 0.01% of the thorium from a solution containing 116 g/liter Th, 6.2 N HNO₃, and 3.76 x 10⁶ c/m/ml Pa-233. A total of 250 ml of this solution was passed through the column at an average flow rate of 1.08 ml/min; protactinium adsorption was constant throughout the run. The protactinium was eluted with 0.5 M oxalic acid, 80% in the first 25 ml of eluant at a flow rate of 0.5 ml/min, and only 4% in the next 25 ml. Qualitative tests indicated that the elution can be improved by increasing the residence time of the eluate in the column. Preliminary experiments gave no indication of the ultimate capacity of the unfired Vycor for protactinium. The maximum adsorption measured was 6 µg of Pa-233 (120 mcuries) per gram of glass.

FLUORIDE VOLATILITY PROCESSING

Pilot Plant. In two runs, TU-9 and 10, 40-kg charges of nonirradiated fully enriched zirconium-uranium alloy fuel were processed with HF at flow rates of 150 and 180 g/min, respectively. Dissolution rates for the two runs were essentially equal, 2.9 and 2.2 kg/hr for 90 and 100% completion, respectively. Corresponding HF utilization efficiencies were 16.6 and 21.1%, for total dissolution times of 20.0 and 18.8 hr. Nonrecoverable uranium losses were 1.36 and 0.89 g.

Although initial uranium concentrations in the fluorinator feed salt were identical, fluorination of the TU-9 salt to < 10 ppm U required only 100 min at a fluorine flow rate of 6 std liters/min compared to 123 min at 6 and 13-18 std liters/min in TU-10. Temperature-zoned absorber performance was satisfactory in both runs. Waste salt recoveries for both runs were 100 ± 5%. A complete uranium balance was not made due to system holdup. At the end of the normal dissolution, 4 hr of additional HF flow at 40 g/min was used to solubilize residual metallics, and visual examination of the vessel after run TU-9 showed essentially clean surfaces.

Run TU-9 was completed without incident. Operational problems in run TU-10 included a bad compressor bearing, leak in the HF flow control

valve, lower than normal heated-duct temperatures, and a UF_6 product line plug. The dissolver off-gas system performed well during both runs at recycle HF flow rates of approximately 350 g/min. A cursory visual inspection of the system after run TU-10 showed no massive deposits or accumulations of off-gas solids. The off-gas filter showed no pressure drop increase during either run, and has now been in service for six consecutive runs without cleaning or discharge of the Yorkmesh cartridge.

Development. Laboratory studies indicated that pure fluorine in place of gaseous HF is not feasible for the dissolution of zirconium-uranium alloy fuel in fused salts. In 36-32-32 mole % LiF-NaF-ZrF₄ salt at 500°C, Zircaloy-2 dissolution rates were 0.5-1.5 mil hr⁻¹ with high-purity fluorine in a 1-in.-dia reactor at a flow rate of 100 ml min⁻¹. However, when 30% HF was used with the F₂ or the salt was presaturated with HF, dissolution rates were 10-11 mil hr⁻¹. The addition of ~1000 ppm FeCl₃ at 500, 600, and 700°C, respectively, increased the rates with no HF and with high-purity fluorine to 5, 6.5, and 8.5 mil hr⁻¹. Attempts to promote the direct gas phase reaction between fluorine and metal failed even at 700°C. Ignition of Zircaloy-2 with fluorine resulted in some melting only when the metal sample was incompletely submerged in the fused salt.

The addition of gaseous HCl to the HF did not increase the dissolution of Zircaloy-2 fuel in fused 36-32-32 mole % LiF-NaF-ZrF₄ at 500°C. In individual tests in a 1-in.-dia reactor with 100-0, 100-100, and 0-100 ml min⁻¹ mixtures of HF and HCl, rates were 10.5, 11, and 2 mil hr⁻¹. These data indicate that the high reactivity of HCl for zirconium alloy (Zircex-type process) is hindered by conversion of the volatile ZrCl₄ to the nonvolatile ZrF₄.

Processing of graphite-10% UO₂ fuels by burning with fluorine in fused salt does not appear attractive on the basis of one test. A small explosion occurred in a small amount of residue left after a run in which the dissolution rate in 36-32-32 mole % LiF-NaF-ZrF₄ salt at 500°C was 58 mils hr⁻¹ with 100 ml min⁻¹ fluorine flow rate. This dissolution rate includes much material that either disintegrated or re-formed as sooty material on the side of the reactor.

In further studies zirconium oxide was dissolved in fused salt by HF at rates about twice as great as for zirconium metal under similar conditions. Preliminary chemical analyses of the film formed on partially dissolved oxide indicated that an intermediate oxyfluoride may be formed.

MECHANISMS OF SEPARATIONS PROCESSES

Simulated ORNL low-activity-level waste, containing 3.3 ppm of Ca^{++} and 10^{-2} M NaOH (pH 11.8) and tracer Sr^{89} - Sr^{90} - Y^{90} was decontaminated from the strontium in a 6-in.-i.d. countercurrent foam column. Decontamination factors, which were 500-5000 with aqueous flow rates of 8-18 gal ft⁻² hr⁻¹ and $(3.8 \text{ or } 7.6) \times 10^{-4}$ M sodium dodecylbenzene sulfonate surfactant, decreased with increasing flow rate, which should be maximized, and with increasing surfactant concentration, which should be minimized. Analytical and graphical methods were derived for correlating decontamination factors, single stage separation factors, aqueous throughput, and volume reduction in a countercurrent foam separation column and are being used to calculate optimum decontaminating conditions.

The heights of transfer units for either isotopic exchange or stripping of strontium were determined in the above column for 7×10^{-4} M sodium dodecyl benzene sulfonate, 10^{-3} M NaOH, and about 10^{-6} M $\text{Sr}(\text{OH})_2$ with Sr-89 tracer, and liquid feed rates of 20-40 gal ft⁻² hr⁻¹. Values based on the liquid phase (HTU_x) were 3-4 in. for 18 in. of foam in the column when air was introduced through a porous stainless steel gas sparger and 1-3 in. for 24 in. of foam and 1-2 in. for 4-11 in. of foam with a spinnerette sparger consisting of 1794 50- μ -dia holes. The difference is due to foam condensation and channeling with the sintered sparger caused by relatively irregular bubble size. Strontium concentration variations from top to bottom in the liquid and foam phases were factors of 1.6-8 in the isotopic exchange runs, compared to 250-500 in the stripping runs.

In extension to acid concentrations > 5 M of an earlier study on the extraction of nitric acid by tributyl phosphate-diluent solutions, acid activities measured at 25°C by a transpiration technique in the range 5-15 M showed good precision.

SOLVENT EXTRACTION STUDIES

In radioactive cell tests of the chemical flowsheet proposed (ORNL-3211) for final-cycle purification of plutonium from Purex LBP solution by tertiary amine nitrate extraction, operation was excellent. Plutonium recovery was also excellent, but γ decontamination factors were 100-500, at least 100-fold lower than needed, and than obtained in tests with tracer Zr-Nb and with dissolver solution mixed fission products. The results strongly indicate that the Purex extraction product contained a significant concentration of more extractable Zr-Nb species, and feed pretreatment will therefore be required. The flooding capacity of pulsed columns ($A/O = 4.1$) was determined to be $> 2400 \text{ gal ft}^{-2} \text{ hr}^{-1}$ for a compound extraction-scrub column with sieve plates (0.125-in.-dia holes, 10% free area), operated with the organic phase continuous at 30 cycles/min. The stripping capacity ($O/A = 5$, aqueous continuous) was $540 \text{ gal ft}^{-2} \text{ hr}^{-1}$ for the sieve plate column and $440 \text{ gal ft}^{-2} \text{ hr}^{-1}$ for a nozzle plate column at 35 cycles/min.

Tracer strontium extraction from 4 M NaNO_3 by di(2-ethylhexyl)-phosphoric acid and its sodium salt in benzene indicated that $E_{\text{Sr}} = [\text{Sr}]_{\text{org}}/[\text{Sr}]_{\text{aq}} \propto [\text{H}^+]^{-2}$ up to 15% sodium form of the reagent and $E_{\text{Sr}} \propto \Sigma$ reagent concentration at all ratios of Na form to total reagent. Equilibrium curves ($\log [\text{Sr}]_{\text{org}}$ vs $\log [\text{Sr}]_{\text{aq}}$) with $\text{NaR}/\Sigma\text{R}$ constant at levels from 0.1 to 1.0 had slopes of 1 at low $[\text{Sr}]_{\text{org}}$. The highest organic/Sr ratio varied from 2.4 to 1.6. The data indicate that, at low total strontium and pH, strontium is extracted, releasing two H^+ ions and forming a mononuclear compound in the organic phase, and that the organic phase either presents an average of two exchange sites per molecular unit to the strontium or extracts it into a highly polymerized species which remains polymerized.

In further testing of alkylbenzenes for possible use as diluents for organophosphorus extractants, benzenes substituted at two points (diethyl- and diisopropylbenzene, tetrahydronaphthalene) were less stable on exposure to 2 M HNO_3 than the corresponding monoalkylbenzenes. Iso chain branching in the monoalkylbenzenes appeared preferable to normal, secondary, or tertiary.

CHEMICAL APPLICATIONS OF NUCLEAR EXPLOSIONS

Hydrogen consumption for the reduction of MgSO_4 decreased from 2.8 to 2.6 moles per mole of MgSO_4 as the temperature was increased from 734 to 784°C but for reduction of CaSO_4 was constant at 4.0 moles per mole of CaSO_4 from 885 to 915°C. The quantity of SO_2 produced during MgSO_4 reduction increased by a factor of 1.5 as the temperature increased from 734 to 784°C. Kinetic studies showed the reduction of MgSO_4 and of CaSO_4 by H_2 to be autocatalytic.

Samples of NaCl and MgSO_4 which had been shocked with high explosive to a few kilobars at Frankford Arsenal were analyzed for chemical decomposition. Determination of the pH and hydroxyl content of water solutions of the samples showed only 0.01% decomposition of NaCl and no detectable decomposition of MgSO_4 .

MWG:mrh

INTERNAL DISTRIBUTION

1. F. L. Culler
2. R. E. Blanco
3. J. O. Blomeke
4. J. C. Bresee
5. K. B. Brown
6. F. R. Bruce
7. D. E. Ferguson
8. M. W. Gerrard
9. H. E. Goeller
10. A. T. Gresky
11. W. H. Lewis
12. M. J. Skinner
13. E. G. Struxness
14. W. E. Unger
15. M. E. Whatley
16. R. G. Wymer
- 17-18. Central Research Library
19. Document Reference Section
- 20-31. Laboratory Records
32. Laboratory Records(RC)

EXTERNAL DISTRIBUTION

33. P. C. Aebersold, Washington AEC
34. B. Anderson, COO
35. E. L. Anderson, Jr., Washington AEC
36. F. P. Baranowski, Washington AEC
37. W. Belter, Washington AEC
38. S. Bernstein, UCNC, Paducah
39. L. P. Bupp, HAPO
40. J. T. Cristy, HOO
41. F. R. Dowling, Washington AEC
42. A. Friedman, Washington AEC
43. R. R. Hayward, AI
44. K. K. Kennedy, IDO
45. S. Lawroski, ANL
46. J. A. Lieberman, Washington AEC
- 47-48. J. A. McBride, ICPP
49. B. Manowitz, BNL
50. R. B. Martin, OROO
51. J. W. Morris, SRP
52. H. Pearlman, AI
53. A. A. Schoen, OROO
54. J. M. Simmons, Washington AEC
55. C. M. Slansky, ICPP
56. C. E. Stevenson, IDO
57. V. R. Thayer, du Pont, Wilmington
58. L. Topper, NYOO

EXTERNAL DISTRIBUTION (Cont'd)

- 59. A. F. Voigt, ISC
- 60. F. M. Warzel, ICPP
- 61. T. R. Workinger, Washington AEC
- 62. L. L. Wyman, NBS
- 63-77. DTIE
- 78. Research and Development Department, ORO