CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

OAK RIDGE NATIONAL LABORATORY LIBRARIES
3 4456 0548845 1

ORNL-TM-245

COPY NO. - 17

DATE - 6/1/62

CHEMICAL TECHNOLOGY DIVISION

MONTHLY REPORT FOR MAY 1962

F. L. Culler, Jr.

ABSTRACT

Process development studies are reported on Chemical Applications of Nuclear Explosions; Power Reactor Fuel Processing (Corrosion Studies, Shear-Leach Process, Solvent Extraction Studies, and Thorium Dicarbide Hydrolysis Studies); Chemical Engineering Research; Fluoride Volatility Processing (Corrosion and Laboratory Studies); Ion Exchange Technology; Mechanisms of Separations Processes (Foam Separation and Thermodynamics of Solvent Extraction); Process Chemistry of Uranium and Thorium; and Solvent Extraction Research.

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.

OAK RIDGE NATIONAL LABORATORY LIBRARIES

3 4456 0548845 1

CHEMICAL APPLICATIONS OF NUCLEAR EXPLOSIONS

Deuterium exchange with hydrogen of water was near statistical at plasma jet temperatures of 10,000-12,000°K for 40-100 msec residence time of the gaseous mixture. Three determinations were made with a D_2/H_2O mole ratio of 1.3 and deuterium enrichments of 49.1, 50.0, and 51.7 atom % D.

The stoichiometry of the reaction of $CaSO_4$ with H_2 varied slightly with the mass of $CaSO_4$ used in fixed bed tests, indicating diffusion-controlled side reactions. At 885°C, the mole percentages of sulfate decomposing to form H_2S with 2.5- and 5.0-g samples of $CaSO_4$ were 4.1 and 2.0, respectively. The bulk of the sulfate was converted to CaS (>95%). Increasing the reduction temperature from 885 to 915°C increased the conversion of sulfate to H_2S from 2.0 to 2.5 mole % and decreased the conversion of SO_2 from 1.5 to 1.1 mole %. Thermodynamic calculations of the species formed by reduction of $CaSO_4$ and $MgSO_4$ by hydrogen agreed with the experimentally observed products of the reductions.

POWER REACTOR FUEL PROCESSING

Corrosion Studies. Specimens of 1100 and 6061 aluminum and type 309 SNb stainless steel were corroded at overall maximum rates of 0, 0.1, and 0.3 mil/mo, respectively, in exposures of 192, 312, and 312 hr in refluxing 23 M HNO_3—1 M HF. The addition of 50 g of uranium and 20 g of graphite per liter of solution increased the corrosion of the 309 SNb stainless steel to 24.7 mils/mo in 96 hr exposure but had no detectable effect on the corrosion of either type of aluminum.

Unwelded specimens of Corronel 230 were corroded at maximum overall rates of 2.1, 62.8, 60.3, and 172.9 mils/mo in exposures of 257, 103, 103, and 89 hr, respectively, in refluxing 4 M HNO_3—0.3 M HF, 4 M HNO_3—5 M HF, 10 M HNO_3—1 M HF, and 10 M HNO_3—5 M HF. The attack was an acid etch in all cases.

Titanium-45A was corroded at maximum rates of 82.5 and 62.3 mils/mo in 48-hr exposures in initial Darex solutions at 87°C to which 0.005 M $Na_2B_4O_7$—0.01 M HBF_4—0.01 M $ZrO(NO_3)_2$ and 0.005 M $Na_2B_4O_7$—0.01 M HBF_4—0.04 M $Al(NO_3)_3$, respectively, had been added. When the additives were

0.0025 M $Na_2B_4O_7$—0.01 M HBF_4—0.04 M $Al(NO_3)_3$, maximum rates were 15.6 and 11.6 mils/mo for 72 and 168 hr exposure, respectively.

Shear-Leach Process. The shear lubrication piping was modified to a system consisting of three manifold sections for more efficient operation. The fourth and last porcelain-filled Yankee prototype fuel assembly containing external ferrules was sheared into 1/4-in. sections without difficulty.

Further particle-size measurements on sheared pieces of porcelain-filled ORNL Mark I prototype fuel assemblies showed that <9520-μ (~3/8 in.) fractions of 1/4, 5/8, and 1.5 in. sheared lengths constituted 69, 21, and 6.6%, respectively, of the total particles, and fractions <44 μ were 5.2, 3.0, and 0.9%, respectively, of the total particles produced. Stainless steel and braze metal particles in the fractions <9520 μ were 33.3 and 2.6% of the total metal from 1/4- and 5/8-in. sheared lengths, respectively, with stainless steel comprising 33.1 and 2.57%, respectively, of the total metal. The amount of porcelain in the <9520-μ fractions were 93, 46, and 12% of the original amount from the 1/4-, 5/8-, and 1.5-in. cuts, respectively; porcelain constituted >99% of the material in the <590-μ fractions from all sizes sheared. Visual comparison of the sheared pieces >9520 μ indicated that a sheared length of ~9/16 in. would probably be optimum.

Solvent Extraction Studies. The distribution coefficient of uranium between 0.6 M $Al(NO_3)_3$ and 2.5% TBP in diethyl benzene decreased from ~0.4 with un-degraded solvent to ~0.2 with solvent boiled 4 hr in 2 M HNO_3 and washed with carbonate. The degraded solvent contained materials that reacted as ~0.1 M acid in titration with caustic. Stirring the solvent 16 hr with feed solution containing 350 g of Th and 5 g of U per liter, 0.8 M Al, and 0.1 N a.d. did not noticeably decrease extraction.

A countercurrent batch extraction of uranium with 2.5% DSBPP-DEB from aqueous solution containing 5 g of U and 10 g of Th per liter, 1.0 M $Al(NO_3)_3$, and 0.1 N a.d. resulted in a decontamination factor from thorium of $>2 \times 10^4$ and a 0.03% uranium loss. A similar experiment with 2.5% TBP-DEB as extractant and 1.5 M $Al(NO_3)_3$ in the feed resulted in a decontamination factor from thorium of 2.5×10^3 and a uranium loss <0.01%.

Thorium Dicarbide Hydrolysis Studies. Hydrolysis of thorium dicarbide in water at 80°C yielded, per gram of sample, 68 ml (STP) of gas consisting of 78% free hydrogen, 1.5% methane, 6% ethane, 1.4% ethylene, 5% acetylene, 1.8% butenes, 3.5% of unidentified compounds in the C_4 region of the spectrum, and small quantities of saturated C_2-C_8 compounds. Of the 7.55 mg-atoms of total carbon (0.4-0.9 mg-atom of free carbon) in each gram of the original carbide, 1.56 mg-atoms were found as gaseous hydrocarbons and 3.41 in a water-insoluble wax; the remaining carbon presumably goes to nonvolatile, water-soluble compounds, which have not yet been isolated. Thorium dicarbide, like uranium dicarbide, appears to yield predominantly nonvolatile carbon products.

CHEMICAL ENGINEERING RESEARCH

The flow capacity of nozzle-plate pulsed columns (organic continuous) for a modified Purex flowsheet, with first cycle uranium product as feed without intercycle evaporation, was lower than with standard Purex, probably because of the higher ratio of dispersed to continuous phase flow (A/O of 1.5 vs 0.45) and lower density of the aqueous phase at the feed point where flooding occurred. The uranium production capacity was only 40% of that of standard Purex because of the lower flow capacity and lower uranium concentration in the feed (65 vs 320 g/liter).

FLUORIDE VOLATILITY PROCESSING

Corrosion. In the highly corrosive 50.5-37.0-12.5 mole % NaF-LiF-BeF_2 melt at 650°C, Alloy 79-4 (79 wt % Ni, 4% Mo, balance Fe) was more resistant to HF than either Inor-8 or several other experimental alloys of nickel and various combinations of Mo, Fe, V, and/or Al:

	Max Penetration Rate, mils/mo	
Alloy	Wt loss data	Micrometer measurements
Alloy 79-4	4.08, 8.02*	23, 23*
Inor-8	23.23, 12.85*	81, 107*
90% Ni-10% Mo	23.68, 2.19*	75, 15*
85% Ni-10% Mo- 5% Fe	17.16, 11.45*	70, 38*
86% Ni- 5% Mo- 4% Fe-5% V	16.28, 17.90	171, 111
82% Ni- 8% Fe-10% V	17.18, 22.62	46, 61
86% Ni-14% Al	Specimen completely severed	
84% Ni-13% Al- 3% Si	Section nearly dissolved	

*First number from test with fresh salt and 2nd number from repeat test with same salt; others were duplicate tests.

The HF flow rate in the 93-hr test averaged 9.3 g/hr. The melt composition and temperature combination was chosen for its high corrosivity to provide accelerated test conditions.

Laboratory Studies. Niobium, a possible constituent of reactor fuels, forms a volatile fluoride, NbF_5, b.p. 229°C. Niobium metal was hydrofluorinated in 31-24-45 mole % $LiF-NaF-ZrF_4$ at rates of 4-6 mg cm^{-2} min^{-1}. Observations indicated that an intermediate fluoride, possibly NbF_3, formed in the presence of excess metal or in the presence of undissolved uranium or zirconium. The material was bluish and had a low solubility in the fused salt. On prolonged hydrofluorination, the blue material disappeared and volatilized as NbF_5.

In two tests, the product NbF_5 was trapped from an HF stream on NaF at 350°C. This temperature was chosen to minimize the formation of NaF-HF complex. In one case, 11.4 g of NbF_5 was absorbed on 92 g of 1/8-in. NaF pellets, with a trapping efficiency of 95.4%. In the second test, with 88 g of 12-20 mesh NaF, the trapping efficiency was 100%, 97.3% being collected on the first half of the bed and 2.7% on the second half. The results may indicate formation of the complexes $NaNbF_6$ and Na_2NbF_7 reported in the literature.

ION EXCHANGE TECHNOLOGY

Ten to 20% of Dowex 50W resin samples decomposed and dissolved or became suspended in water when irradiated to 0.75-0.77 x 10^9 r (2.0-2.1 watt-hr per gram of dry resin). Both the specific wet resin volume, i.e., ml wet resin/g dry resin, and the moisture content increased 10-15%. The resin lost 40-50% of its original strong acid capacity but gained ~5% weak acid capacity. The radiolytic loss of sulfur was calculated to be 1.0-1.2 atoms/100 ev. A comparison of the titrated strong-acid capacity and actual sulfur determination of the exposed resin showed that only 75-80 of the sulfur remained on the polymer as the active sulfonate (HSO_3^-) group. Partially completed analyses of the collected effluents indicated that degradation products included sulfate, sulfonate, and oxalate in the acid form. Effluents concentrated by vacuum distillation showed evidence of an increasing quantity of suspended solids <10 μ as the resin exposure time increased.

For these studies the hydrogen form of Dowex 50W X-8, X-12, X-16, and X-20 was exposed in a system of flowing demineralized water (<1 μmho/cm) in a 10,000-curie cobalt-60 source. The resin column effluent was passed through (1) a series of cells that continuously monitored the pH and electrical conductivity and (2) a strong-base anion-exchange resin column that concentrated the sorbable cation-exchange resin degradation products. In order to obtain a solution concentrated enough to analyze for radiation degradation products, this stream was collected and its volume decreased 100-fold by vacuum distillation at room temperature.

MECHANISMS OF SEPARATIONS PROCESSES

Foam Separation. Concentrations of calcium, which interferes with removal of strontium from low-activity wastes, and magnesium were decreased to 1-2 ppm, as Ca, corresponding to 96% removal, in a gently agitated sludge chamber. Precipitation was with 5×10^{-3} M each of NaOH and Na_2CO_3 and coagulation with 1 or 2 ppm Fe^{3+}; retention times in the sludge bed were 35 min and flow rates ~8 gal hr^{-1} ft^{-2}. The resulting solution contained only 0.2 ppm Ca + Mg as solids. Waste d.f.'s were 20-200 from Sr and 10-40 from Cs. Addition of Grundite clay to the alkali chamber in ~0.5-g amounts at ~12-hr intervals over a 2-day run, to an average of ~0.5 lb/1000 gal, gave a further d.f. from Cs of >10. Passage of 4000 column volumes of the solution plus contained solids from the sludge column through a column of the cheap ion—exchange mineral Decalso did not improve the d.f. from Cs but increased that from Sr by a factor of ~50. Cesium broke through to 1% at ~5000 column volumes and to 10% at ~6500 column volumes.

A 0.4-in.-dia cyclone tested as a foam breaker had a feed capacity of 14 liters/min for an inlet/outlet pressure ratio of 4. The uncondensed foam volume varied from <0.2% for dry foam to 4% of the feed foam volume for wet foam. Foam densities initially were as much as six times the steady-state values for the same conditions with recycle of the condensed foam. Bubble sizes from the spinnerette gas distributor showed little variation for gas velocities of up to 500 cm/sec in the 50- or 80-μ-dia holes, but increased as the hole gas velocities increased above this value.

The bubble size distribution from the spinnerette with 50-μ-dia holes was well represented by normal distributions (avg dia = 0.53 mm, σ = 0.08 mm) for hole gas velocities below 500 cm/sec. The spinnerettes at higher velocities and porous metal or fritted glass gas spargers at all velocities gave size distributions with a tail of large bubbles which did not fit a normal curve. HTU values at higher column throughputs were 0.8-1.1 in. at 120 gal hr^{-1} ft^{-2} and 1.4 in. for one run at 160 gal hr^{-1} ft^{-2} for stripping of Sr-89 with 7×10^{-4} M dodecylbenzenesulfonate.

Thermodynamics of Solvent Extraction. Vapor pressures of nitric acid in water were measured by a transpiration technique at 25°C over the concentration range 2-16 M. Activity coefficients calculated from these data were combined with literature data on partial pressures of this acid over aqueous solutions measured over the concentration range 10 to 23.867 M (100% HNO_3) and with literature data on freezing points of solution containing 0 to 3 M acid. From this combination a consistent set of activity coefficients of HNO_3 from 0 to 100% acid were calculated, and the thermodynamic constant, K, for the dissociation reaction $HNO_3 \rightleftharpoons H^+ + NO_3^-$ was calculated for two standard states: (1) K = 1000 ρ/63.016 = 23.867 in molar units when the stoichiometric activity coefficient $y_{s,o}$ = 1 for the pure acid. In this standard state, the stoichiometric activity coefficient for nitric acid infinitely dilute in water is 0.00925; ρ is the density of pure HNO_3, 1.504 g/ml, and 63.016 its molecular weight; (2) if the activity coefficient of the acid infinitely dilute in water is defined as unity, then $K = 1.169 \times 10^4$ and the activity coefficient of pure acid, $y_{s,o}$ = 22.1.

PROCESS CHEMISTRY OF URANIUM AND THORIUM

Effluents from uranium mills normally contain certain radioisotopes, e.g., Ra-226, at concentrations too high to legally permit their direct discharge to the environment. Radium was effectively removed from simulated lime-neutralized acid waste by adsorption on some natural and synthetic zeolites, including clinoptilolite, Decalso, and Linde Molecular Sieves 13X9X and AW-500. In a column test with clinoptilolite, the effluent activity was still less than 5% of that of the head solution after

passage of 2200 column volumes of solution. The radium was almost completely eluted with ~10 column volumes of 1.8 M NH_4Cl—0.2 M HCl.

SOLVENT EXTRACTION RESEARCH

In further study of the stability of sulfuric acid-treated Amsco 125-82, some of the solvent was scrubbed with concentrated acid at room temperature, made to 1 M with TBP, and then boiled 24 hr under total reflux with an equal volume of 2 M nitric acid. The Zr-Nb extraction ability of this material was approximately the same as fresh, undegraded 1 M TBP Amsco.

Extraction of a number of metals from 0.5-10 M HCl and LiCl—0.2 M HCl (0.5-10 M total Cl) was surveyed with typical primary, secondary, tertiary, and quaternary amines in diethylbenzene diluent. In general, extractions increased with increase in chloride concentration and were higher for the quaternary (Aliquat 336) than for the other amines. The maximum coefficients (0.1 M amine) were ~10,000 for Fe(III), ~100 for vanadium(V) and vanadium(IV), 0.35 for scandium, and 0.6 for chromium(III).

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. M. J. Skinner
12. E. G. Struxness
13. W. E. Unger
14. M. E. Whatley
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, 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 (ANL)
57. V. R. Thayer, du Pont, Wilmington
58. L. Topper, NYOO
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 Division, OROO