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CHEMICAL TECHNOLOGY DIVISION

MONTHLY REPORT FOR SEPTEMBER 1961

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ABSTRACT

Process development studies are reported on Power Reactor Fuel Processing, Fluoride Volatility Processing, Solvent Extraction Research, Spectrophotometric Studies of Solutions at Elevated Temperatures and Pressures, and Chemical Applications of Nuclear Explosions.

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POWER REACTOR FUEL PROCESSING

Beryllium- and Beryllium Oxide-containing Fuels. GCRE fuel pellets (70% UO_2--30% BeO) were completely dissolved in 10-14 hr in boiling 8 M HNO_3 containing 0.5-0.8 M NaF. With no fluoride in the dissolvent, complete dissolution required at least 30 hr. The final solutions contained about 4 g of uranium per liter.

Uranium-Graphite and Uranium Carbide Fuels. Leaching of graphite--8% UO_2 fuel specimens for 4 hr with boiling 90% HNO_3 showed that the recoveries increased from 98.2 to 99.2% as the terminal uranium concentration in the leach solution was decreased from about 50 to 10 g/liter.

SiC-coated Pebble Bed Reactor prototype fuel spheres containing ThO_2-UO_2-impregnated graphite were mechanically cracked and reacted with boiling 90% HNO_3 at 60°C. After 3.7 hr of exposure, the fuel was disintegrated to 60% <4 mesh. Uranium loss after washing was ~6%. The 30-mil SiC coating material was uniformly distributed among the sieve fractions; residual uranium concentration was higher in the 100/325 mesh fraction than in the +100 mesh material.

Uranium monocarbide containing about 17 mole % uranium metal reacted with water at 80°C to produce an average of 1.71 mmoles of H_2, 2.83 mmoles of methane, and 0.48 mmoles of carbon, and 1.29 mmoles of monatomic hydrogen as saturated C_2 to C_6 aliphatic hydrocarbons per gram of sample hydrolyzed. The off-gas contained 36% H_2 and 60% CH_4. The original specimen contained 4.03 mmoles of uranium and 3.33 mmoles of carbon by both synthesis and chemical analysis. These data indicate that the principal reactions occurring in the hydrolysis of U-UC mixtures are:

$$U + 2H_2O \longrightarrow 2H_2 + UO_2 \cdot xH_2O$$

$$UC + 2H_2O \longrightarrow CH_4 + UO_2 \cdot yH_2O$$

where the degree of hydration of the UO_2 is unknown.

Solvent Extraction. In a preliminary test with short decayed irradiated thoria fuel, all the thorium and uranium and 85% of the protactinium were extracted from a nitrate fuel solution. Decontamination factors were 4×10^4 from rare earths, 1.4×10^3 from Ru, and 100 from gross γ in the first extraction cycle. If these results are typical, it will be possible to process 90-day-decayed Consolidated Edison thorium reactor fuel with an anticipated recovery of 99.9% of the fissionable and fertile material and remove >90% of the high neutron-capture fission products.

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About 90% of the protactinium was removed from a solution containing 2×10^5c min^{-1} ml^{-1} Pa, 220 g/liter Th, 15 g/liter U, 0.09 M Al, 0.04 M F, and 9-10 M HNO_3 by adsorption on crushed unfired Vycor glass. About 59, 61, and 67%, respectively, of the protactinium was adsorbed on 0.5, 1, and 2 g of glass stirred with 50 ml of the solution for 15 min. A column packed with fired Vycor did not remove protactinium from the solution.

The use of tertiary amines as a Pu extractant is being studied. After plutonium has been partitioned from uranium with trilauryl amine, it is stripped with acetic acid which also extracts some nitric acid. In corrosion tests, type 347 stainless steel tubing suffered what appeared to be a mild etch when exposed 96 hr to 1 M HNO_3--3.2 M acetic acid--45 g/liter $UO_2(NO_3)_2 \cdot 6H_2O$. Over-all corrosion rates were 0.02 mil/mo.

Mechanical. Nine NaK-bonded SRE Core 1 fuel clusters, containing 668 kg of uranium, were successfully dejacketed mechanically. A total of 1624 kg of uranium has now been dejacketed and only ~200 kg of the SRE fuel remains to be processed. The experimental production rate was ~6.0 kg U/hr; about three times this rate would be expected from actual assembly line processing with the present equipment. Analysis of NaK eutectic bond indicated a Cs-137 concentration of 2×10^7 to 2×10^8 dpm/ml.

In operability tests with the 250-ton prototype fuel shear, performance was generally satisfactory; however, minor modifications planned to optimize operations include improving the operation of the feed mechanism and fuel assembly length indicator, changing the rubber gag inserts, and remachining the inner gag to facilitate easier removal from the shear.

Zirconium-containing Fuel. Engineering-scale studies on continuous dissolution of simulated highly enriched U-Zr alloy fuels in 6.5 M NH_4F 0.6 to 1.0 M NH_4NO_3 0.1 M H_2O_2 (modified Zirflex) were continued in 6-in.-dia equipment. The process system achieves stability and is easily controlled. Steady-state operation was satisfactory, and a feed/fuel element surface ratio of 0.08 cm/min, the reaction rate was 5.6 mg cm^{-2} min^{-1} and the Zr concentration 70 g/liter. When the feed/surface ratio was decreased to 0.06, the Zr loading increased to 75 g/liter, but the product rate was lower because of a decrease in the reaction rate to 4.5 mg cm^{-2} min^{-1}. Dissolution rates were only slightly affected by removal or reflux of the reaction product NH_3 as NH_4OH.

Dissolution of zirconium in titanium equipment possibly can be accomplished by 3 M HNO_3--0.4 M HBF_4--1.2 M HF--0.46 M $(NH_4)_2Cr_2O_7$. Although in laboratory tests titanium was corroded at 1 in./mo in this refluxing dissolvent, the very high initial corrosion rate decreased very rapidly as zirconium dissolved. At a F/Zr solution mole ratio of 26 with the titanium touching the dissolving Zircaloy-2, the alloy dissolved at 30 mg cm^{-2} min^{-1} and titanium corrosion was not measurable in short-term tests. Without coupling to Zircaloy-2, the titanium corrosion rate was also negligible at a F/Zr ratio of 9, and the Zircaloy-2 dissolved at a rate >20 mg cm^{-2} min^{-1}. The dissolver product was stable at both the boiling point and at room temperature when the zirconium concentration was 0.47 M Zr at a final F/Zr ratio of 6 and when the solution contained aluminum nitrate in equimolar amounts with the free fluoride, i.e., all fluoride in excess of 4 moles per mole of zirconium.

FLUORIDE VOLATILITY PROCESSING

In a revised system for removing entrained fused salt, nickel, and oxides from the hydrofluorinator discharge gas stream installed in the Pilot Plant, the recirculating HF is scrubbed by a condensing fraction of the HF. Tests indicated that the flash cooler is adequately designed and that the scrubbing system performs satisfactorily. In two runs there was no line plugging with solids, and a metal wool filter in the gas stream showed no increase in pressure drop due to solids.

The applicability of the fused salt--HF dissolution system for fuel materials other than zirconium metal is being explored systematically. Massive zirconia plates were dissolved by HF in molten $NaF-LiF-ZrF_4$ at 1.24 and 3.13 mg cm^{-2} min^{-1} with HF rates of 1.9 and 11.3 g/min. The variation in dissolution rates with changing HF flow rate is the same as for zirconium metal. However, it is encouraging that at any given HF mass flow rate the dissolution rate of this oxide is several times that of zirconium metal. A 304 stainless steel tube containing eutectic Na-K was dissolved by HF in fused salt at a wall penetration rate of 2 mils/hr.

Uranium was recovered from Zircaloy-2-clad UO_2 fuel pins, irradiated to 600-1200 Mwd/t and decayed 14 to 28 days, by dissolution in 24-31-45 mole % $NaF-LiF-ZrF_4$ at 650°C with HF at a rate of 10 mg cm^{-2} min^{-1} and fluorination of the melt at 500°C. The chief activity in the UF_6 product of five tests can be attributed to U-237 and a negligible amount of Mo-99. The other short-half-life fission products of interest in these tests were I-131, Te-127, Te-129, and Te-132. The IF_7 and TeF_6 presumably formed in the fluorination step were separated from the UF_6 in the absorption step, indicating no complexing of these materials with NaF.

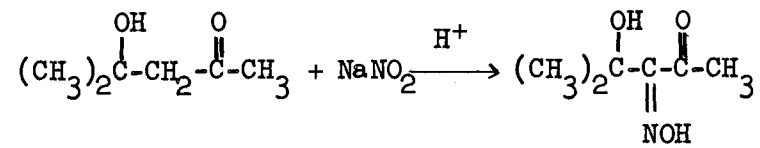
In additional studies on the mechanism of the absorption of UF_6 by NaF pellets, partial differential equations were derived for the concentration of unreacted UF_6 as a function of time and position in a sphere of NaF. The model includes the effects of stagnant gas film, resistance, diffusion rate of UF_6 in the pores of the sphere, reaction rate at the pore walls, and effect of local UF_6 loading on the rate of transport and of reaction at the surface. The equations were converted to finite difference form in preparation for numerical solution, to be followed by experimental checks of the model.

SOLVENT EXTRACTION RESEARCH

Monoalkylbenzenes showed promise as diluents with improved chemical stability for use with organophosphorus extraction reagents, e.g., TBP. In an extraction test where lower Zr-Nb-95 extraction coefficients indicate greater stability, a 1 M TBP solution in n-butylbenzene had an extraction coefficient 1/200 of that of 1 M TBP in Amsco 125-82 after both solutions had been exposed to boiling 2 M HNO_3.

Keto-oximes added to aqueous feed solutions improve separation of uranium from Zr-Nb and Ru in TBP extraction. In batch countercurrent extractions with 1 M TBP-Amsco 125-82 from Zr-Nb-95 tracer solutions, Zr-Nb

extraction was a factor of 170 lower with 0.1 M diacetone alchol + 0.1 M sodium nitrite in the feed. The system is assumed to yield a keto-oxime by the reaction



A chemical flowsheet was proposed for final-cycle plutonium purification by tertiary amine extraction (ORNL-3048) and acetic acid stripping (ORNL-3074). A Purex partitioning-cycle plutonium stream can be accepted as feed with no adjustment other than re-oxidation of plutonium to Pu(IV); sulfate can be tolerated at the levels expected from ferrous sulfamate reductive stripping in the Purex cycle.

Isotherms for extraction with trilaurylamine (TLA) in diethylbenzene from 1.5 M HNO_3, fitted by the empirical equation

$E_a^o(Pu) \approx E_1 [M_{amine} - 3 M_{Pu}]^2$ where E, is defined by $\log E_1 \approx 3.5 - 2.5 \sqrt{M_{SO_4}}$

were confirmed by batch countercurrent demonstration with 0.3 and 0.1 M TLA and simulated feed of 1 g Pu/liter-1.5 M HNO_3-0.03 M $Fe(NH_2SO_3)_2$. Product solution contained 20 g Pu/liter. Zr-Nb tracer in the feed at 7×10^5 γ c min^{-1} ml^{-1} could not be detected in a γ scan of the product. Radiochemical analysis for zirconium in the product showed 116 Zr γ counts min^{-1} ml^{-1}, decontamination factor Pu/Zr = 5×10^4.

SPECTROPHOTOMETRIC STUDIES OF SOLUTIONS AT ELEVATED TEMPERATURES AND PRESSURES

A spectrophotometer system based on the Cary model 14 spectrophotometer was designed by The Applied Physics Corporation to ORNL specifications for operation up to the critical temperature of water and for pressures up to 10,000 psi. A complete cell was fabricated, and extensive tests showed it completely satisfactory for operation up to at least 330°C and 3000 psi. Special features of the system include an automatic digital data readout on IBM cards (or perhaps magnetic tape), a viewing port and mirror for visual observation of the test solution at all operating temperatures, and a vertical slit system for spectral measurements on individual phases of two-phase systems by individual adjustment of the slits. A system for rocking the cells at variable speeds while they are operating at elevated temperature and pressure was designed to permit mixing of the cell contents and equilibration of the gas in the cell over-space with liquid and to remove bubbles that may form on the cell windows. Part I of a report on the problem of the Cerenkov radiation in making spectrophotometric measurements on highly radioactive solutions was issued as ORNL-3180.

A miniature loop system operable up to 150°C and 200 psi for circulating solutions through special cells in a standard Cary model 14 spectrophotometer was designed and constructed by ORNL, and set up for preliminary testing external to the spectrophotometer system. It can be used in the standard Cary

model 14 spectrophotometer system without modification of the spectrophotometer. The auxiliary system for digital output from the wavelength and absorbancy information includes circuitry that prevents output of spectral data which the recorder (single pen) is changing between ranges of absorbancy and a photoelectric pulse generator for digitizing the wavelength information.

CHEMICAL APPLICATIONS OF NUCLEAR EXPLOSIONS

A number of solids that may be present in rock salt were tested as catalysts for vapor phase exchange in the H_2-H_2O-HTO system. The measured values were compared with the equilibrium exchange that can be obtained using platinum as the catalysts for the same reaction. The chlorides were not very effective catalysts, while oxygenated salts and oxides in the form of large crystals were moderately effective:

Substance	Surface Area, m^2/g	% of Equilibrium Exchange Achieved with Pt Catalysts
NaCl	0.015	0.65
$CaCl_2$	0.39	6-7
K_2SO_4	0.007	42.5
Silica gel	520	44
Al_2O_3	6.7	77
K_2CO_3	0.073	80
"Drierite" ($CaSO_4$)	9.7	95

The results are consistent with the view that exchange involves adsorption of one or all of the reactants on a surface containing exposed oxygen atoms. The chloride exchange is believed to involve reversible hydrolysis. Surface area differences apparently affect exchange in some cases.

Studies of the mechanism of the reduction of magnesium sulfate by hydrogen at 750 to 800°C indicated that the sulfate is first reduced to the sulfite, which thermally decomposes to MgO and SO_2 at the reduction temperature. Sulfur dioxide reacts very rapidly with hydrogen at these temperatures to produce H_2S, H_2O, and free S when catalyzed by the MgO. All steps in the proposed mechanism have been checked by direct experiment except formation of $MgSO_3$. Experiments at 650°C indicated that the decomposition is more rapid than the sulfate reduction and thus the sulfite cannot be detected directly.

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