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CHEMICAL TECHNOLOGY DIVISION

MONTHLY REPORT FOR DECEMBER 1961

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ABSTRACT

Process development studies are report on Fuel Cycle Development and Fuel Preparation, Power Reactor Fuel Processing, Radioactive Waste Treatment and Disposal, Protactinium Chemistry, Equipment Decontamination, Spectrophotometric Studies of Solutions at Elevated Temperatures and Pressures, Thorium Oxide Studies, U-232 Preparation, Transuranium Element Studies, and Fission Product Recovery.

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FUEL CYCLE DEVELOPMENT AND FUEL PREPARATION

Development studies on the sol-gel process for preparing highly compactable 3 wt % uranium-thorium oxides were continued. Oxide fragments, homogeneous with respect to the U/Th atom ratio and satisfactory for vibratory compaction (787 g/cc, ~87% of theoretical density), were obtained by addition of uranyl nitrate (50 g U/liter solution, with an N/U mole ratio of 4, to thoria prepared by steam denitration at 425°C without subsequent air calcination in the 15-kg batch calciner. Mixed sols adjusted to pH 3.2-3.5 with ammonia gave gels of uniform composition on evaporation. Sizing in the easily reducible evaporated-gel step gave mixtures which were vibrated to bulk densities of 8.68 and 8.63 g/cc. Dried gels calcined in air by increasing the temperature to 1150°C, at a rate of 300°C/hr and holding for 4 hr, and then reduced at 1150°C 4 hr in 4% hydrogen-argon gave uranium-thorium oxides of >9.9 g/cc particle densities and packed densities >8.5 g/cc. For reduction to an O/U ratio of <2.02, 3-5 hr was required.

In engineering development, the 15-kg ThO_2 batch rotary steam denitrator was operated without mechanical difficulty in eight runs. Control of dispersibility and N/Th ratio of the ThO_2 product was demonstrated in the last four runs. Sol-gel product prepared as a 10-kg batch was compacted to 8.9-9.0 g/cc by vibratory compaction in tubes 0.5 in. dia and 4 ft long.

POWER REACTOR FUEL PROCESSING

Beryllium- and Beryllium Oxide-containing Fuels. A simulated GCRE fuel element about 8 in. long, weighing 36.58 g, was digested with boiling 3 M HNO_3—4 M HCl for 9 hr. The Hastelloy-X cladding was penetrated at the end of 3 hr, after which the UO_2 was rapidly leached from the UO_2-BeO pellets. Eighty per cent of the Hastelloy-X and 20% of the BeO was dissolved. About 0.2% of the uranium originally present in the BeO pellets remained undissolved and was not removed by washing with hot water.

Chop-leach Process. Scouting tests indicated that shearing into the flat side of a fuel assembly with a stepped blade rather than into a corner is unsatisfactory because of tube spreading and drag back. A straight movable blade was unsatisfactory because chunks of tubes rather than discrete pieces were produced.

In a life test, a 4-in.-dia stainless steel bellows for a 4-in. flapper valve to be used as a seal between the shear and the feeder, conveyor and leacher failed at 35,400 cycles, equivalent to a life of about 4 years. Test stand evaluation of a duplicate bellows gave an acceptable life of 50,000 cycles.

To ensure that a batch of fuel is covered by the acid leachant in each flight of the leacher, the leacher must be reversed an amount equal to the angle of repose each time a batch of fuel is moved forward one flight. A 28° angle of repose was measured for a 36-kg batch of chopped porcelain-filled ORNL Mark I fuel assemblies and a 9.7-kg batch of solid 1/2-in.-dia stainless steel rods 1 in. long and of 32° for 2.5 kg of empty ORNL Mark I sheared tubes while being transported through the inclined rotary leacher.

Corrosion. Rolled and welded Haynes 21, heat-treated after being welded at 2100°F and quenched, was corroded in boiling Darex dissolver solution at maximum rates of 2.35 and 2.03 mils/mo for water- and air-quenched specimens, respectively. These rates are about one-third those obtained on non-heat-treated specimens but are higher by a factor of ~2.5 than those obtained on the (apparently) cold-rolled, unwelded material obtained from Battelle Memorial Institute. Some intergranular attack was observed in the heat-affected zone near the welds. Similar heat-treatment of welded Haynes 25 increased the corrosion rate from about 0.31 to 16 mils/mo in initial Darex dissolver solution.

Titanium-45A, Corronel 230, and 1100 aluminum were corroded at maximum rates of 0.18, 1.79, and 127 mils/mo, respectively, in 24 hr exposure to boiling 20 M HNO_3. The titanium rate decreased to 0.07 mils/mo in 168 hr exposure. The vapor phase specimen of Corronel suffered intergranular attack after longer exposure.

Nichrome V exposed to CCl_4--N_2 at various temperatures between 550 and 725°C was corroded at rates which increased from about 2 mils/mo at 550°C to about 1100 mils/mo at 725°C.

Graphite-base Fuels. UO_2-graphite fuel specimens, containing from 0.7 to 12% uranium, and up to 0.45% iron as impurity, were burned in oxygen at 750-850°C, and the oxide residue was digested 4 hr with boiling 10 M HNO_3. The uranium loss to the nitric acid-insoluble residue decreased from 2 to 0.002% as the U/Fe weight ratio in the specimen increased from 5 to 45.

In the reaction of type GBF graphite with concentrated HNO_3, the mixture of water-soluble organic acids produced after 211 hr digestion contained 50% mellitic acid (benzenehexacarboxylic acid). Infrared analysis of the mixture confirmed the presence of the carboxyl groups and showed only a small amount C-H bonding, as would be expected if the mixture consisted primarily of benzene polycarboxylic acids. No evidence for the existence of nitro groups in the acids was obtained.

An irradiated (nvt = 10^{15}) graphite compact containing about 4% uranium as pyrolytic-carbon-coated uranium carbide particles was leached three times, 6 hr each, with boiling 90% HNO_3, to determine the integrity of the coatings. Although the matrix was completely disintegrated, a total of only about 1.5% of the uranium was solubilized, indicating that nearly all the fuel particles remained intact during irradiation. The cylindrical specimen was 1 in. dia and 1.5 in. high, and 3.5 ml of acid per gram of specimen was used.

SRE Fuel Dejacketing. All SRE mechanical dejacketing equipment was removed from Cell A of Bldg. 3026 for decontamination and storage for possible future use. Decontamination of the cell by remotely spraying the interior surfaces of the cell with steam, water, detergent, and oxalic acid solution and vacuuming up dried particulates decreased contamination from a general cell reading of >10 r/hr to ~80 mr/hr.

Metallurgical examination of the embrittled type 304 stainless steel fuel jackets showed evidence of hardening by cold working but no carbide precipitation or nitrogen absorption. A uranium-stainless steel eutectic was found which randomly covered very small areas of the internal surfaces of the jackets. The formation of this alloy accounts for some of the difficulties encountered in dislodging slugs from the jackets.

Solvent Extraction. In laboratory tracer level tests at least 90% of the Pa was extracted with the U and Th by TBP from <1 N acid synthetic Thorex solution. Decontamination factors from high neutron cross section fission products were ~100.

An unirradiated sample of Pebble Bed Reactor graphite-base fuel was leached with 90% HNO_3 containing fission products to synthesize irradiated fuel solution. Less than 1% of the activity was adsorbed by the disintegrated graphite. During evaporation of the leach solution to remove excess acid, Ru volatilization increased as the U concentration in the pot increased, but totaled only about 1% of that in solution. Uranium was extracted from the diluted feed with 10% TBP--Amsco with decontamination factors of 5000, 1000, 600, and 10^5 from gross γ, Ru, Zr-Nb, and rare earth elements, respectively.

Addition of 0.03 M fluoride to an NH_4NO_3 scrub solution increased thorium removal from a synthetic U-233 product to the limits of analytical detection. Fluoride was less effective with an $Al(NO_3)_3$ scrub.

Zirflex Process. Four prototype PWR blanket rods, Zircaloy-2 clad UO_2, irradiated 191-356 Mwd/ton and decayed 2 years, were declad with boiling 6 M NH_4F—1 M NH_4NO_3 in an average time of 1.5 hr. The final F/Zr mole ratio in the solution was 7. The end cap residues were ~5 g per pin. Maximum U and Pu losses were 0.04 and 0.22%, respectively. The core pellets were largely shattered, with <1% smaller than 10 mesh.

Core dissolution in 5 M HNO_3 was complete in ~40 min, giving a <4 M HNO_3 solvent extraction feed containing 100 g U/liter. The solid residue from decladding and core dissolution, <0.001% of the initial core weight, consisted of traces of Ca, Fe, Cr, and Sn; U and Pu were not detected.

RADIOACTIVE WASTE TREATMENT AND DISPOSAL

Engineering, Economic, and Hazards Evaluation. The minimum salt mine area required to dissipate heat from stored mixed fission product waste depends on (1) concentration and age of the fission products; (2) maximum permissible temperatures in the waste and salt; (3) heat dissipation characteristics of the waste, salt, and air (if any) between the waste and salt; and (4) way in which the waste is disposed of. For calculations, amounts and concentrations of fission products were taken as those corresponding to Purex and Thorex liquid or calcined solid wastes produced by

processing of 1500 tonnes/year of 10,000-Mwd/tonne uranium and 270 tonnes/year of 20,000-Mwd/tonne thorium, and maximum permissible temperatures as 200°F for liquid disposal, and 1650°F in the waste and 400°F in the salt for calcined solid disposal.

For liquid disposal on the floor of a salt mine the net area requirements dropped from 35 to 10.5 to 5.2 acres/year as the waste age increased from 0.3 to 3 to 30 years, respectively, after reactor discharge. For gross area requirements these numbers should probably be doubled to allow for only 50% excavation of the mine area. For calcined solids disposal in racks above the floor the mine area requirements were a factor of 2.3 less than for liquids, the factor being not quite equal to a ratio of 2.6 between maximum permissible temperature rises for the two cases because of poorer heat dissipation by salt at higher temperatures. For this case the minimum age from reactor discharge to burial varied from 0.3 to 8 years.

PROTACTINIUM CHEMISTRY

Absorption spectra of 15 and 34 N H_2SO_4 solutions of protactinium were essentially identical, with a single, rather broad peak at 2250 A. In 5 N H_2SO_4 the spectrum was significantly different, with no peak but with increasing absorption down to the limit of measurement at about 1970 A.

Distribution coefficients (o/a) for amine extraction of protactinium from sulfuric acid decreased as the acid concentration increased from 5 to 15 N, from 5×10^3 to $\sim 10^2$ for Primene JM-T, from 300 to 4 for N-benzylheptadecylamine, and 20 to 0.1 for Alamine 336. All amines were 0.1 M in diethylbenzene, and the protactinium concentration was 0.08 mg/ml in the sulfuric acid solutions before extraction.

EQUIPMENT DECONTAMINATION

Carbon steel in helium at EGCR temperatures (about 1050°F) is very sensitive to oxygen contamination in the helium, quickly acquiring a blue oxide color or film when exposed to small traces. Oxygen residues in the EGCR during startup, or subsequent air inleakage, may therefore impede decontamination because of the necessity of dissolving the oxide film. Laboratory-produced thin blue oxide films were removed in 1 hr, with acceptable corrosion rates, by a boiling 10% solution of a proprietary

inhibited phosphoric acid. Thicker films were more resistant. Helium containing no oxygen was slightly reducing to the film at 1050°F, probably because of a trace of hydrogen.

Oxalate-acetate-peroxide preparations continued to give good results in the low-corrosion decontamination of several fission products baked onto carbon steel in helium. When the pH was lowered from 4.5 to 2.5, corrosion was accelerated by H_2O_2 up to 0.6 M, and inhibited above 0.6 M. Decontamination by the lower pH solution at 60°C instead of 95°C continued to prove feasible, provided the H_2O_2 was increased to prevent corrosion.

SPECTROPHOTOMETRIC STUDIES OF SOLUTIONS AT ELEVATED TEMPERATURES AND PRESSURES

Design and drawings of the spectrophotometer and the associated auxiliary and control systems for study of solutions at high temperatures and pressures were completed, as well as specifications for the fabrication, testing, and installation of the system at ORNL. It is anticipated that with this system it will be possible to make spectral measurements up to the water critical point (~372°C) in both water and deuterium oxide systems.

Construction and installation of the miniature loop system and its related control instrumentation were completed. The loop was designed for use with an unmodified Cary Model 14PM spectrophotometer to operate at pressures up to 200 psi and temperatures to 150°C.

In further work on mathematical resolution of spectral fine structure and complex overlapping absorption spectra, programs for the IBM-7090 computer are being prepared, and codes for the Oracle and IBM-704 are being converted for operation on the IBM-7090 machine. An automatic digital data-output system was constructed and tested and is now operating in conjunction with the spectrophotometer. A preliminary discussion of the system has been written, which includes an IBM punched-card output of the spectrophotometric data with the wavelengths and absorbancy information punched in pairs. Data may be obtained at wavelength intervals as close as 1 A. The card-decks of the decimal spectral data are obtained simultaneously with the strip chart record.

THORIUM OXIDE STUDIES

Several different thoria powder and pellet preparations (50 g total) are being irradiated in D_2O in the LITR at 260°C and a flux of ~3 x 10^{13} n cm^{-2} sec^{-1} in an autoclave especially designed for multiple-sample irradiations. The preparations are separately contained in thin-walled stainless steel tubes but share a common gas phase, and in some cases a common liquid phase, through the sintered stainless steel filter plugs used for the tube closures. An oxygen overpressure of 290 psi at room temperature was provided.

In the first 185 days of a projected 6-7 months' irradiation, 14% of the initial O_2 added has been consumed, and 50 psi of radiolytic gas has been produced. The estimated total heat to be removed has risen from an original value of 800 to 920 watts owing to the buildup of U-233.

TRANSURANIUM ELEMENT STUDIES

Variables were investigated in the 2-ethylhexylphenylphosphonic acid vs. 2 M HCl system which is proposed for separation of californium and curium. Addition of 10% 2-ethylhexanol, a degradation product, decreased the distribution coefficients a factor of 10 but did not change the californium-curium separation factor. Aliphatic diluents gave higher distribution coefficients than aromatic, and extraction increased with alkyl branching on the benzene ring. Hydrochloric acid distribution coefficients over the range 1-10 M HCl were <0.001. Californium and curium distribution coefficients were inversely proportional to the cube of the hydrogen ion concentration over the range 1-4 M HCl and were directly proportional to the 6th power of the hydrogen ion concentration over the range 6-10 M HCl. The californium-curium separation factor was about 100 over the range 1-4 M HCl and about 10 over the range 6-10 M HCl.

The extractability of various corrosion and fission products was determined for the 2-ethylhexylphenylphosphonic acid vs. 2 M HCl system. Fe^{3+}, Zr^{4+}, and Sn^{2+} were extracted with californium, while Sr^{2+}, Cu^{2+}, Ru^{3+}, Ni^{2+}, Cr^{3+}, Co^{2+}, Mn^{2+}, Cd^{2+}, and Zn^{2+} remained in the aqueous phase. Stripping the californium with 6 M HCl stripped out only Sn^{2+}, leaving Fe^{3+} and Zr^{4+} in the organic phase.

A corrosion study indicated that α activity at 2 watts/liter had no direct effect on corrosion rates of Hastelloy B, Hastelloy C, titanium 45A, tantalum, Zircaloy-2, and glass in chloride solutions. However, secondary effects, from the H_2O_2 produced by radiolysis of water, were accelerated corrosion rates for Hastelloy B and C and much greater corrosion resistance of titanium 45 A in 6 M HCl. Zircaloy-2 and tantalum showed no effect due to radiolysis.

U-232 PREPARATION

An ion exchange method for separating uranium and protactinium was tested on a small scale with 208 mg of Pa-231 irradiated as oxide to 2.5×10^{18} nvt and decayed 30 days. The oxide was dissolved in 8 M HCl--0.4 M HF to a Pa concentration of 10 g/liter Pa and passed through a 2-ml column of Dowex 1-4X (50-100 mesh) resin. The loaded column was washed with nine displacement volumes of 8 M HCl--0.4 M HF. The combined feed and wash effluents contained most of the protactinium and <7% of the U-232. The U-232 product eluted from the resin with 0.5 M HCl contained 73 μg of U-232 and protactinium content was estimated as <300 μg of Pa. The U-232 in the protactinium product and Pa-231 in the uranium product were below the limits of detection by the analytical method used. The irradiated protactinium oxide had apparently sintered, so that dissolution required heating for several hours at 80°C. Instead of the 150 μg of U-232 calculated for the sample, only about 80 μg was found in the oxide solution. Additional irradiations are being made in a monitored flux to determine the reason for this discrepancy.

Solvent extraction of uranium from mixed HCl-HF solutions by either tributyl phosphate or trilaurylamine appears satisfactory for final uranium purification. Uranium and protactinium distribution coefficients between 40% TBP in Amsco and 8 M HCl--0.5 M HF were found to be ~50 and 0.003, and between 0.1 M trilaurylamine in diethylbenzene and 7.5 HCl--0.9 M HF, 140 and 0.002, respectively.

FISSION PRODUCT RECOVERY

The solvent extraction flowsheet (ORNL-2993) for recovery of fission product strontium and mixed rare earths with di(2-ethylhexyl)phosphoric acid was successfully demonstrated in continuous mini-mixer-settler equipment with Purex 1WW waste solution from Hanford. In the first cycle >99% of the strontium was recovered with decontamination factors of 20 from Cs and Zr-Nb, 180 from Ru, and $>2 \times 10^3$ from Fe, a performance as good as or better than predicted on the basis of tracer runs. Approximately 90% of the total rare earths was extracted and ~90% of that extracted was stripped, for an overall recovery of ~80%. In the second cycle, ~99% of the total rare earths was extracted and separated from strontium. Strontium was recovered from the second cycle raffinate in a third extraction cycle, yielding a product solution containing ~1 g of Sr, 1 g of Ni, and 20 g of Na per liter. Overall Sr recovery was ~98% with overall decontamination factors (based on first cycle feed) of $\geqslant 1.7 \times 10^3$ from rare earths, $\sim 10^5$ from Zr-Nb, $\sim 3 \times 10^3$ from Cs, and 10^4 from Ru.

Extraction of nitric acid and iron sulfate from Purex 1WW solution with amines is being studied as a means of producing a feed solution highly amenable to strontium and cesium recovery by solvent extraction. In preliminary tests with a primary amine, ~90% of the nitrate and iron and most of the sulfate were removed from synthetic 1WW solution in a single contact.

In preliminary tests, sodium dinonylnaphthalene sulfonate in hexone and p-dodecylphenol in xylene selectively extracted cesium from simulated low acid (formaldehyde-treated) waste, complexed with tartrate and adjusted to high pH's. p-Dodecylphenol also had separation factors >15 from Na and other alkali metals. Both reagents had separation factors >100 for Cs from Zr-Nb, Ru, and rare earths and >20 for Cs from Fe and Al and were readily stripped with dilute nitric acid.

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