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CHEMICAL TECHNOLOGY DIVISION

MONTHLY REPORT FOR OCTOBER 1961

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ABSTRACT

Process development studies are reported on Fuel Cycle Development and Fuel Preparation, Power Reactor Fuel Processing, Radioactive Waste Treatment and Disposal, Equipment Decontamination, Thorium Oxide Irradiations, and Transuranium Element Studies.

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FUEL CYCLE DEVELOPMENT AND FUEL PREPARATION

The sol-gel procedure for preparation of dense, compactible UO_2-ThO_2 was simplified. Addition of 3-7 wt % uranium to thoria sols as $UO_2(NO_3)_2 \cdot 6H_2O$ rather than as ammonium diuranate produced a homogeneous mixture of U and Th in the sol and final fired product. During precalcination of dried gels rates of temperature rise of 100 vs 300°C/hr, maximum temperature up to 1050°C, and times at maximum temperature of 1-17 hr had no significant effect on the final fired particle density if the powder is air-fired at 1200°C for 4 hr. Uranium in valence states other than U(IV) can be reduced in the final powder by heating in atmospheres of argon, argon-4% hydrogen, nitrogen, and pure hydrogen; all appeared to be equally effective in decreasing the O/U ratio. Thus it may be possible to remove the H_2 firing step from the flowsheet.

In nine batch 5-kg scale runs by the sol-gel flowsheet products were test-vibrated to packed densities of 8.4 to 8.8 g/cc (with eight samples >8.5 g/cc) in 5/16- and 1/2-in.-dia stainless steel tubes. Variations in the N/Th ratio of 0.09-0.13, evaporation of sol beds of 3/4 to 2 in. depth, and air-calcination temperatures of 500-700°C for thoria prior to sol preparation appeared not to be critical with respect to obtaining packed densities of 8.5 g/cc or greater.

Eight fuel element specimens for irradiation under GCR conditions in the ORR poolside facility were prepared by pneumatic-vibratory packing of sol-gel-prepared UO_2-ThO_2 (2.5 and 3.9 wt % enriched uranium) to bulk densities of 8.58 ± 0.03 g/cc in 5/8-in.-dia stainless steel tubes containing a 1/8-in.-dia molybdenum axial thermowell and to 8.75 ± 0.08 g/cc in 1/2-in.-dia stainless steel tubes.

POWER REACTOR FUEL PROCESSING

BeO-UO_2 Fuels. The initial dissolution rate of sintered 5% UO_2—95% BeO in HF-HBF_4 solutions containing up to 5 M HBF_4 increased from 0 to 1.4 mg cm^{-2} min^{-1} as the HF concentration was increased from 0 to 15 M regardless of the HBF_4 concentration. GCRE fuel pellets, 70% UO_2—30% BeO, dissolved completely in <14 hr in boiling 8 M HNO_3 containing 0.5-0.8 M NaF. The final solution contained about 4 g of uranium per liter.

Corrosion Studies. Welded specimens of Haynes 25 exposed to boiling 5 M HNO_3—2 M HCl for 264 hr were corroded at maximum rates of 0.31 mil/mo vs 3.1-10.0 mils/mo for Haynes 21 exposed 192 hr. Grain boundary attack was observed on both alloys. The poor behavior of Haynes 21 is believed to be due to the mill anneal which was given this alloy.

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In N_2 saturated (at 25°C) with CCl_4 Haynes 25 was corroded at rates varying from about 600 mils/mo at 727°C to 10 mils/mo at 580°C. The plot of log corrosion rate vs $1/T$ was very nearly linear. Corrosion of Haynes 25 appeared to be uniform at all temperatures.

Titanium was corroded at a maximum rate of 0.03 mil/mo in 144 hr exposure to boiling 21.5 M HNO_3 containing 50 g of uranium and 20 g of graphite per liter.

Graphite-base and Uranium Carbide Fuels. In experiments with unirradiated 1.5-in.-dia Pebble Bed reactor fuel spheres, >99% of the uranium and thorium were recovered by leaching with boiling 90% HNO_3 provided that neither the spheres nor the fuel particles were coated with SiC. Uranium recoveries from spheres coated with pyrolytic carbon were high only after the spheres were roughly crushed. Both SiC- and pyrolytic-carbon-coated particles were inert to 90% HNO_3.

In engineering-scale tests uranium loss was not acceptable in semicontinuous runs in which -4 mesh graphite-base fuel containing 2.6% U was leached in 90% HNO_3 at 60°C. The leaching cycle consisted of a 2-hr batch leach followed by a 4-hr leach in flowing acid, and a final water wash. Uranium losses to the residue were 1.5, 1.6, 0.61, and 0.56% at flow rates of 0.52, 0.91, 1.52, and 2.21 bed volume changes per hour, respectively.

In studies on the application of the chloride volatility method to processing of graphite-base fuels, chlorine at 750°C removed 97% of the U_3O_8 from 7% uranium-graphite specimens in 1 hr. Further treatment at this temperature had no effect. Treatment of one sample at 750°C with mixed Cl_2 and O_2 volatilized 98.4% of the uranium in 20 min. The graphite did not ignite.

In scouting studies on hydrolysis of uranium carbide containing considerable amounts of U_2C_3 (some UC_2 and either U metal or UC) the gaseous products at 80°C consisted of 58% hydrogen, 2% methane, 26% ethane and a complex mixture of 24 additional saturated and unsaturated hydrocarbons.

Mechanical. Mechanical dejacketing of the SRE Core 1, NaK-bonded stainless steel—clad uranium fuel, was successfully completed. A total of 1780 kg of uranium slugs, 0.75 in. o.d. by 6 in. long, was dejacketed, steam cleaned, recanned in aluminum, and stored to await shipment to SRP for processing. The over-all average processing rate, based on actual operating time, was ~6 kg U/hr. The temperature of a can of 12 slugs stored in air was 2.5°F above the storage room temperature of 87°F.

In shearing studies, preliminary tests of an outer gag (fuel assembly clamp) faced with rubber and a metallic inner gag contoured to the shape of a sheared assembly were very encouraging. The stepped moving blade of the shear has now made about 800 cuts against stainless steel-jacketed porcelain-filled Mark I propotype assemblies with no signs of wear.

Preliminary design of the shear-leach complex auxiliary equipment is essentially complete, and design of the electrical control circuit for manual and automatic operation of the conveyor-feeder and leacher was completed.

Solvent Extraction Studies. The flowsheet used for processing MTR fuel in the Idaho Chemical Processing Plant includes an aluminum nitrate solution scrub. Substitution of this with a 4 M HNO_3 scrub improved decontamination in laboratory experiments, but modification of the present plant equipment would be required for equivalent results in the plant.

The amount of protactinium removed from nitric acid solutions containing 6×10^5 c m^{-1} ml^{-1} Pa by 15-min batch contact with 10 g of 100-200 mesh unfired Vycor glass per liter increased from 82% in 0.1 M HNO_3 to a maximum of 94% in 6-8 M HNO_3. With 6 M HNO_3 adsorption was more than 90% complete in the first 5 min. The presence of 50 g of thorium per liter decreased the adsorption from 0.1 M and 8 M HNO_3 to 45 and 86%, respectively, but increased the adsorption from acid-deficient solutions from 0 to 45%.

Zirconium-containing Fuel. Continuous dissolution of Zircaloy-2 in refluxing 3 M HNO_3—0.4 M HBF_4—0.6 M Cr(III)—0.4 M Cr(VI)—0.46 M Zr in a titanium dissolver appears practicable. Dissolution rates were 10 mg cm^{-2} min^{-1} and corrosion rates, 0.0 mil/mo in short tests. Addition of aluminum nitrate to complex the fluoride ion gave a stable product solution containing 0.36 M Zr. With the dissolvent 16 M HNO_3—2.6 M F—0.025 M HBF_4—0.4 M Zr the titanium corrosion rate was also 0.0 mil/mo, but Zircaloy-2 dissolution rates were only 3 mg cm^{-2} min^{-1}.

RADIOACTIVE WASTE TREATMENT AND DISPOSAL

Low-Level Waste Treatment. An additional demonstration run on process waste water in the semi-pilot plant facility gave effluent with <10% of the mpc for >1500 bed volumes of waste treated. Total hardness in the clarifier overflow averaged 20 ppm. The early breakthrough in an earlier run is believed to have been due to carbonate deficiency in the feed, which resulted in saturation of the resin with calcium. This will be forestalled in the pilot plant by continuous analysis of the effluent for hardness.

Installation of the 10-gpm low-activity-waste pilot plant is complete, including an enclosed type 3 FLC Oliver vacuum filter substituted for an Eimco-Burwell plate-and-frame filter to concentrate the sludge effluent from the clarifier. Approximately 300 hr of nonradioactive processing was accomplished with ORNL tap water, with the objectives of orienting personnel, optimizing operating procedures, and testing equipment.

High-activity. In nine calcination runs, with both batch and continuous evaporation of feed, in engineering-scale (8-in.-dia by 90-in.-high) stainless steel calcination pots, simulated Purex and TBP-25 wastes were fed, after evaporation, to the calciner at average rates of 25-31 liters/hr when filling

the pots to 90% of capacity. In two runs where organic phosphates were present, average feed rates were a factor of 4 lower because of excessive foaming in the calciner.

Oxides from TBP-25 waste were incorporated into glassy materials at 875-1000°C by addition of phosphate with borate and lead oxide fluxing agents. The solids, 2.36-2.84 g/ml density, represented waste volume reduction factors of 7.2-8.4. The condensates from batch evaporations of TBP-25 waste made 2 M in sodium hypophosphite contained 0.48 and 0.71% of the original ruthenium; less ruthenium, 0.68 vs 2.18%, was released when the feeds were made 0.25 M in PbO than when made 0.25 M in $Pb(NO_3)_2$. The chief gaseous product from the reaction between iron or aluminum nitrates (1-2 M) and phosphorous acid (1 M) appears to be nitric oxide. The best catalysts found for the reaction between nitrate and phosphite ions were silver, mercuric, and palladium ions. Vapor-liquid equilibrium conditions were investigated for simulated TBP-25, Darex, and Purex waste solutions as a function of acid and salt concentrations, and densities of the solutions were measured as function of temperature and pressure.

The economics of disposal of high-activity waste in salt by (1) liquids in rooms with recessed floors, (2) pot calcination vessels in racks above the floor, and (3) pot calcination vessels in holes in the floor is being studied. The gross mine space area required for case 1, calculated by the infinite-slab-heat method, varied from 67 to 10 acres/year for decay times of 0.33 to 30 years.

EQUIPMENT DECONTAMINATION

Oxalate-peroxide with either acetate or citrate as buffers decontaminated stainless steel from Cs-137 by factors of 1000-2000 in 20 min at 95°C. The production of hazardous peracetic acid during the use of oxalate-acetate-peroxide mixtures for decontamination was negligible. The stainless steel samples were contaminated with carrier-free Cs-137 under simulated EGCR conditions by exposure to cesium vapor volatilized at 750°C in helium from a mixture of Cs-137 chloride and metallic calcium. The peroxide mixture at 85-95°C was a good low-corrosion rust remover and decontaminant for miscellaneous rusty hand tools, but large quantities of rust shortened the life of the solution to about 2 hr.

In initial tests on decontamination from ruthenium oxalate-peroxide, 1 and 2 hr at 60°C and pH 2.5 was equivalent to 0.5 and 1 hr, respectively, at 95°C and pH 4.3. At 65°C and pH 2.5, corrosion was severe. In decontamination of the Pebble Bed Reactor, pyrolytic-carbon-coated UC_2 dust will apparently have to be removed solely by detergent action except where dissolution in fused $KOH-KNO_3$ is practicable.

THORIUM OXIDE IRRADIATIONS

Determination of pycnometric densities in H_2O of Code P-82 thoria pellets indicated that irradiation has no particular effect on pellet density and that long-term autoclaving under water at 250°C causes some of the internal pores to become surface connected. The density of the as-received pellets was 9.16 g/cc. After 3 months' irradiation in the LITR (7×10^{16} fissions/g), pellet densities were 9.45 and 9.34 g/cc, before and after drying, respectively. Corresponding values for the control pellets were 9.68 and 9.40 g/cc. The density of pellets autoclaved only 2 days at 250°C and not dried was 9.25 g/cc.

The surface area of the irradiated pellets was 1.48 m^2/g as opposed to the 0.01 m^2/g obtained with the original pellets. However, in a 1-hr wear test (standard spouting bed test) the irradiated pellets lost only 0.013% weight, a factor of more than 10 less than that lost by the original pellets. The surface area after the wear test was 1.54 m^2/g.

The crystallites in thorium oxide powders irradiated dry in the LITR (at <300°C) appeared to be approaching an equilibrium size of 500 to 600 A (10^6-10^7 Th atoms) as measured by x-ray diffraction line broadening. The original crystallite sizes of the oxides fired at 650, 800, 900, 1100, and 1500°C were 120, 220, 500 1140, and >2000 A, respectively. After 1.5×10^{18} fissions/g exposure the crystallite sizes were 265, 400, 560, 540, and 850 A, respectively. Annealing the 1100 and 1500°C fired materials did not change the line broadening. Therefore 10^6-10^7 thorium atoms appear to be displaced by each fission in the thorium oxide.

TRANSURANIUM ELEMENTS STUDIES

Results of fire hazard tests on o-xylene in a glove box indicated that a simple water sprinkler back-up system will be adequate for fire suppression. In a test for explosive conditions at a box temperature of 100°F (open cup flash point of o-xylene is 75°F) no audible explosions occurred, but the pressure rose 7 to 8 in. H_2O in <1 sec. The fires snuffed out even when 5 cfm purge and/or an open glove port existed.

In extraction of americium from 11 M LiCl into 30% Alamine 336 in diethyl benzene at 25°C, equilibrium was achieved within 10 sec. However, in scrubbing the pregnant organic with 11 M LiCl, about 1 min was required at 25°C and 10 sec at 60°C. A 0.81-in.-i.d. pulsed extraction column with nickel as a stand-in for actinides showed up to 4 stages in 25 in. length.

Plutonium for the neutron-cross-section program will be purified by dissolving highly irradiated Pu-Al alloy in nitric acid and isolating the plutonium on anion exchange resin. From the column effluent, 6 M HNO_3—0.75 M $Al(NO_3)_3$ containing Am, Cm, fission products, Na, Fe, Ni, and Hg, the Am, Cm, and rare earths can be recovered by anion exchange resin from neutral aluminum

nitrate solution. Synthetic column effluent evaporated to a temperature of 140°C and diluted with water was acid-free, and was stable at room temperature with up to 2.7 M $Al(NO_3)_3$. In tests at 70°C with 15 column displacement volumes of feed containing Eu tracer on Dowex 1-10X (50-100 mesh) resin, Eu losses from 2.7 M $Al(NO_3)_3$ feed were 23.2% for a flow rate of 4 ml cm^{-2} min^{-1} and 0.12% for a flow rate of 2 ml cm^{-2} min^{-1}. At a flow rate of 2 ml cm^{-2} min^{-1} Eu losses were 0.12, 0.27, 2.20, and 16.2% for $Al(NO_3)_3$ feed concentrations of 2.7, 2.3, 2.0, and 1.8 M, respectively.

Separation of americium and curium by chromatographic elution from Dowex 50-10X (100-200 mesh) resin with 0.5 M ammonium alpha hydroxyisobuterate at pH 4.0 improved with increasing resin volume. With a 5-ml column, 70% of the Cm was free of americium, and with a 250-ml column, 95%.

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