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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, Protactinium Chemistry, Thorium Oxide Studies, Transuranium Elements, U-232 Preparation, and Fission Product Recovery.

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FUEL CYCLE DEVELOPMENT AND FUEL PREPARATION

Four hundred grams of dense 4 wt % Pu-ThO_2 was prepared by the sol-gel process. Four 11 x 5/16-in. test capsules with a bulk density of 7.5 g/cc were fabricated by vibratory compaction for irradiation in the NRX reactor, and are now being leak-tested.

The feasibility of preparing dense, compactable 3 wt % uranium-thorium oxide by a simplified modification of the sol-gel process was demonstrated on a laboratory- and a 7-kg scale. The modification consisted in adding a thoria powder or water slurry to a heated, agitated solution of uranyl nitrate and nitric acid whose nitrate and uranium contents had been adjusted to give an optimum NO_3/ThO_2 mole ratio and a specified U/Th mole ratio. Particles of the product formed had densities >9.9 g/cc, desirable size, a total 1200°C vacuum gas release of <0.01 cc/g, and were vibratory-compacted to bulk densities >85% of theoretical.

In 12 sol-gel process development runs, 15-kg scale, in the rotary denitrator ThO_2 products were obtained which were dispersed into sols of excellent appearance and free of undispersible residue. The calcination and reduction furnace and procedures developed are believed adequate. In development of methods for determining the nitrate/ThO_2 requirement for maximum dispersion and stabilization of uranium-thorium oxide sols, it was shown that, at the optimum ratio, approximately half the active ThO_2 surface sites in a 2 M sol, at pH ~3.1, are occupied by nitrate. The available active surface sites can be estimated from crystallite size as measured by x-ray line broadening. A convenient method of determining the net nitrate demand was found to be digestion of the ThO_2 in a slight excess of HNO_3, and back-titrating to a pH of 3.1 with ammonia.

Eight 11-in.-long fuel pins vibratorily compacted with sol-gel UO_2-ThO_2 have completed one year, 10,000-17,000 Mwd/ton, irradiation in the NRX. Six 39-in.-long specimens for the replacement holder in the NRX were gamma-scanned for density variations, x-rayed, and wound with a wire spiral to prevent bowing from coolant loss.

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POWER REACTOR FUEL PROCESSING

Corrosion. Titanium exposed to Darex dissolver solution for 72 hr at 87°C and containing 0.0025 M $Na_2B_4O_7$ and 0.01 M HBF_4 showed corrosion rates for the vapor, interface, solution, and condenser areas of 3.0-5.5, 53.1-55.6, 90.8-92.6, and 0.02-0.09 mils/month, respectively. When the solution also contained 0.04 M Al^{3+}, corresponding rates were 0.62-1.2, 10.6-12.3, 15.3-15.6, and 0.03 mils/month.

Specimens of Ni-o-nel exposed in the vapor above refluxing solutions of 6, 8, 10, 12, and 15.6 M HNO_3 for 648 hr were corroded at overall rates of 1.8-1.9, 3.0-3.4, 6.7-7.2, 20.2-20.5, and >37 mils/month, respectively. Intergranular attack was noted after 168, 120, 120, 48, and 48 hr, respectively. In the vapor above refluxing 4 M HNO_3, maximum overall rates for 1344 hr exposure were 1.3 mils/month for Ni-o-nel vs. 0.6 for LCNA. In both materials the onset of grain boundary attack was between 192 and 360 hr. Condenser specimens showed rates of <0.1 mil/month in both cases. These results indicate the necessity for potential users of Ni-o-nel to test this material under the exact conditions expected in their process. The results of cyclic Sulfex or Zirflex tests may not be so pessimistic as those reported for tests with nitric acid alone.

Unwelded specimens of Type 6061 aluminum and welded specimens of type 309 SNb stainless steel exposed in refluxing 23 M HNO_3-1 M HF for 144 hr were corroded at apparent maximum rates of 0.1 and 0.6 mil/month, respectively. Rates were essentially constant over the complete exposure period. All the aluminum specimens gained weight except those exposed in the vapor phase.

Shear-Leach Process. The shear section of the shear-leach machanical complex checkout runs, including evaluation of the electrical circuitry for proper articulated operation, was completed. Chemical processing equipment installation is complete except for insulation of steam and acid lines. Wear studies of the gibs and liners and the stepped blade are still in progress and operation of the shear and all its auxiliaries continues to be very satisfactory.

Thirteen ORNL Mark I porcelain-filled prototype fuel assemblies were sheared into 1/2-, 5/8-, and 1-1/2-in. sections for further particle size distribution and blade wear measurements. The Squarkeen No. 3 stepped blade shows only slight wear after 4271 cuts on the porcelain-filled fuel assemblies. Wear is primarily by rounding of the leading corners of the center step.

Measurements of ~4-kg batches of 3/4-, 1/2-, and 1/4-in. sheared lengths of porcelain-filled elements assembled with both Nicrobraz-50 and Kanigen-brazed spacer ferrules showed no appreciable difference in the particle size distributions from Nicrobraz-50 or Kanigen-brazed elements. For 1-, 3/4-, 1/2-, and 1/4-in.-long cuts, the fractions of material <9520 μ dia were 11, 16, 33, and 74%, respectively; and for material <44 μ, the fractions were 1.5, 2.4, 4.3, and 5.2%.

The results of shear tests on three porcelain-filled Mark I fuel assemblies with 1/8-in.-thick stainless steel tube sheets located 1/2 in. from each end indicate that it may not be advisable to shear fuel assemblies containing tube sheets in the 250-ton prototype shear. In two of the six cuts the shear blade was passed through the tube sheet. In one cut the tube sheet was cut into two pieces, one of which contained seven tubes and the other 25 tubes. The larger chunk jammed between the adjustable stop and inner gag on the reverse stroke of the ram, resulting in some deformation of the adjustable stop.

Solvent Extraction. The distribution coefficients for thorium between 1 M $Al(NO_3)_3$-0.1 M HNO_3-x M Th and both 2.5% TBP and 2.5% di-sec-butyl phenyl phosphonate were measured. For solutions containing <0.65 M Th the coefficient was larger for the TBP system; for feed containing >0.65 M Th the coefficient was smaller in the TBP system.

In a countercurrent batch extraction of uranium with 2.5% DSBPP in DEB, decontamination from thorium was 10^4 with four extraction and three scrub stages. One volume of feed with the composition 10 g/liter Th, 5 g/liter U, 0.8 M Al, 0.1 N a.d. was extracted with 1 vol of solvent and the loaded solvent was scrubbed with 0.4 vol of 0.8 M Al, 0.1 N a.d.

Zirflex Process. Demonstration of the Zirflex decladding process, including subsequent modified Purex solvent extraction of the core solution, on an engineering scale was completed. In 22 runs with specimens of Zircaloy-clad uranium dioxide pellets irradiated 168 to 17,700 Mwd/ton of uranium, the cladding was removed by 6 M NH_4F-1 M NH_4NO_3 in 2-3 hr. The zirconium end plugs remained. Soluble uranium and plutonium losses to the decladding solution averaged about 0.05%. Centrifugation or filtration of the decladding solution is indicated to remove the 1-2% of the UO_2 present as fines resulting from the fracture of low (93-95%) density pellets; however, high (96%) density pellets produced few UO_2 fines.

Approximately 5 hr was required to dissolve the declad UO_2 core material in 4 M HNO_3 to produce a solvent extraction feed of 100 g of uranium per liter and 3 M HNO_3.

Gamma decontamination factors for the Purex first-cycle uranium and plutonium product streams were 1.3×10^3 and 2.1×10^3, respectively. Pretreatment of the solvent extraction feed with diacetyl monoxime or its degradation product oxalic acid increased these factors 2- to 10-fold.

Extended re-use of 30% TBP in Amsco 125-82 diluent as solvent in a simulation of the extraction-scrub-strip-solvent recovery scheme with 17,000 Mwd/ton feed solutions resulted in the formation of uranium-retaining degradation products in the solvent that could not be removed by the usual solvent recovery procedures of carbonate and nitric acid washing. No degradation was shown when n-dodecane or the commercial equivalent Adakane-A12 was substituted for Amsco 125-82.

RADIOACTIVE WASTE TREATMENT AND DISPOSAL

Engineering, Economics, and Hazards Evaluation. A preliminary conceptual design and cost estimate for a solids disposal facility in salt indicated costs of 6×10^{-3} to 30×10^{-3} mill/kwh_e. Sixty to 85 percent of the total costs were attributable to salt removal, indicating that the best possible estimates of this item will be required for the more detailed final study.

Heat transfer calculations of shipping containers for pot-calcined wastes of various ages showed that as many as thirty-six 6-in.-dia pots of calcined acidic Purex waste can be shipped in a single finned carrier after 2.4 years' decay without mechanical cooling en route. Four 24-in.-dia pots of acidic Purex waste can be shipped, per carrier, after 11 years' decay.

High-level Waste. The thermal conductivities of a phosphate-lead glass were 1.05 and 1.60 Btu/hr.ft.°F at 300 and 1050 °F, respectively. The production of this glass on a semi-engineering scale was accompanied by volatilization of 12.5% of the original ruthenium and physical entrainment of <0.02% of the promethium as determined from counting Ru-106 and Pm-147 tracers.

Simulated Darex waste solution was incorporated into glassy and microcrystalline phosphate and borophosphate solids with softening points of 850-900°C and densities of 2.73-3.75 g/cc, and containing 13.4-32.3 wt % waste oxides, representing volume reductions of 2.9-6.6 fold.

Decreasing the pressure from 750 to 570 mm Hg had little effect on the relative volatilities of ruthenium from 6 M HNO_3. Addition of 0.1 M H_3PO_3 to nitrate solutions of ruthenium chloride and ruthenium nitrosohydroxide with and without salts occurring in waste solutions decreased the ruthenium distillation factor by factors varying from 2920 for 6 M HNO_3 containing ruthenium nitrosohydroxide to 38.3 for simulated Darex waste containing ruthenium chloride.

Process flowsheets and an equipment layout were completed for the Idaho Chemical Processing Plant's Pot Calcination Pilot Plant. A mercury trap for removal of mercury compounds from the calciner off-gas was designed and fabricated, and several welded closures for sealing pots were leak-tested at the Georgia Nuclear Laboratory, showing leak rates <0.02 standard cubic centimeter of helium per year.

Low-level Waste. In the scavenging-ion exchange process for removing radioactive fission products from waste, scavenging was improved by adding $CaCO_3$ to the flash mixer, by either adding 25 ppm of $Ca(OH)_2$ or recirculating sludge from the clarifier. Residual hardness was <18 ppm at 24°C.

Increasing the temperature from 4 to 35 °C had little effect on the caustic-copperas treatment but decreased the residual hardness from 70 to 7 ppm in the lime-caustic treatment. Results with a laboratory-scale clarifier showed that the equipment size may be decreased by a factor of 10-20 over the present pilot plant equipment.

The results of five demonstration runs completed in the Pilot Plant with ORNL process waste water as feed were essentially the same as those obtained previously: Sr-90 d.f. 2000-12,000, Cs-137 d.f. 77-3000. Plant effluent solutions contained <3% of current MPC_w values for all isotopes at the 2000-bed volume level (56,000 gal). A resin column isotope breakthrough run showed a Sr-90 release to plant effluent after 2916 bed volumes.

EQUIPMENT DECONTAMINATION

Oxalate-peroxide buffered with acetate was not unduly corrosive to carbon steel (0.007 mil/hr at pH 4.0, 95 °C) when used as a spray decontaminant, but acetic acid vapors were corrosive to metal not contacted by the spray. Although citrate buffer was corrosive when used in too high a ratio to the hydrogen peroxide (up to 50 mils/hr in 0.4 M oxalate-0.4 M peroxide-0.4 M citrate at pH 4.0 and 95 °C), a citrate-containing solution was developed which had a maximum corrosion rate of 0.003 mil/hr for at least 12 hr at 95 °C, and then passed in 1 hr through a maximum corrosion peak of 0.16 mil/hr. A commonly used alkaline descaling formula, basic versene with triethanolamine, was as effective a decontaminant for Zr-Nb-95, and as ineffective for ruthenium, as was an alkaline proprietary reagent. Oxalate-peroxides are effective on both Zr-Nb-95 and ruthenium, can be handled more conveniently, and present fewer problems in waste disposal.

PROTACTINIUM CHEMISTRY

Protactinium distribution coefficients between aqueous sulfuric acid solutions and N-benzylheptadecylamine dissolved in diethyl benzene were determined under conditions of varying amine and acid concentrations. The coefficients increased approximately linearly with amine concentration up to about 0.1 N, but less rapidly at higher concentrations. They decreased

with increasing sulfuric acid concentration, the decrease being proportional to the 1.5 to 2.0 power of the sulfuric acid concentration between 3.3 and 8 N, and to the 6 to 8 power in sulfuric acid concentrations 9 to 12.5 N. The change in dependence on acid concentration was quite sharp. Distribution coefficients with 0.01 N amine ranged from 147 in 3.3 N H_2SO_4 to 1.82 in 12.4 N acid.

THORIUM OXIDE STUDIES

Irradiation of experiment C-43-6B, inserted in the LITR June 15, 1961, at 2.5×10^{13} n/cm^2·sec is continuing. In this experiment a variety of thorium oxide preparations under D_2O in a single autoclave are separated from each other by thin-walled stainless steel tubes. The preparations include the code P-82 thoria pellets, sintered thoria compacts (prepared by a different method than the P-82 pellets), fired sol-gel thoria particles, fired sol-gel thoria spheres (44-74 μ), arc-fused thoria fragments (44-74 μ), and 1600°C-fired thoria powder (DT-46). The expected duration is 12 months' irradiation at full reactor power, at which time the U-233 content will be 0.5% and the oxides will have received an exposure equivalent to that received in a blanket cycle.

Both wet and dry irradiation appeared to harden the surface of thoria pellets, but when the surface shell was worn away wear rates were similar to those for unirradiated materials. In a standard spouting bed test, wet (260°C) irradiated P-82 thoria pellets showed a 10-fold increase in wear resistance ($\leq$0.01% weight loss per hour) over the control or original pellets in the first 2 hr, but in the next 3 hr, wear rates of the irradiated and unirradiated (original pellets, not autoclaved) were essentially the same, 0.1% weight loss per hour. For the remaining 9 hr the wear rates of the irradiated pellets were about twice as fast as those of the original, i.e. 0.5% weight loss per hour. The weight loss of dry-irradiated (3 months) pellets during the first hour was 0.03%. During the next 3 hr the average weight loss was 0.25% per hour, and for the next 9 hr, 0.32% per hour. The differences between the wet- and dry-irradiated pellets probably reflect a wet-autoclaving treatment rather than a radiation effect.

TRANSURANIUM ELEMENTS

In scouting tests on methods for separating americium and curium, O_3 passed through a solution of 3 M K_2CO_3 in which americium and curium hydroxides had been dissolved rapidly oxidized the americium to AmO_2^{2+}, which formed an intense reddish-brown complex. On standing overnight, the americium was reduced to AmO_2^{+} and precipitated as an insoluble carbonate that contained 80% of the americium and carried <5% of the curium.

Distribution coefficients were about 50 for Ru^{4+} and 0.4 for Ru^{3+} in the Alamine-336-diethyl benzene vs 11 M LiCl system. Between this organic and 6 M HCl, which may be used as a strip, values were 6 for Ru^{4+} and 0.02 for Ru^{3+}. Ruthenium can exist in both valence states in LiCl and HCl solutions.

The extraction positions of californium-einsteinium and fermium were redetermined in the 30% Alamine 336 HCl-DEB from 11 M LiCl system. Results agreed with those reported in ORNL-3185, the positions being Cf > Fm > Es.

The extraction positions of einsteinium and fermium in the 1 M 2-EH(ØP)A-DEB from 2 M HCl were Fm > Es > Cf, and the same as reported in ORNL-3273.

URANIUM-232 PREPARATION

Four products containing a total of 32.7 mg U-232 were prepared by irradiating 7.3 g and 40.8 g of Pa-231 in the ORR and processing each after 45 hr decay and again after 80-90 hr decay. An isotopic analysis has been obtained for only one product, which contained 130 ppm U-233, 90 ppm U-235, and 12,200 ppm U-238.

The irradiated Pa-231 in HCl-HF solution was processed to separate uranium and protactinium. The Pa-231 irradiated 10 hr at a flux of 9×10^{13} $n \cdot cm^{-1} \cdot sec^{-1}$ and decayed 40 hr read 6000 r/hr at about 3 ft. The radiation was primarily from Pa-232 and decayed with the Pa-232 half life of 1.32 days.

The uranium was further purified by either a second anion exchange cycle or by tertiary amine extraction from HCl-HF solutions, with conversion to a nitrate system and extraction of uranium into tributyl phosphate as the final purification step. Assay of the final products by gross alpha and alpha energy determinations showed U-232 providing >96% of the gross alpha radiation. Other alpha activity was primarily from U-232 daughters.

FISSION PRODUCT RECOVERY

In continued studies of o-phenylphenol (OPP) as a cesium extractant, improved results were obtained in a batch countercurrent test by adding acid to the last extraction stage to lower the pH to 6-9. That portion of the OPP which had dissolved in the aqueous phase as the sodium salt redistributed into the organic phase, thereby maintaining it at as high or higher concentration than the initial 1 M feed. This not only avoided excessive loss of extractant but also resulted in considerably higher cesium extraction coefficients in the system than those previously obtained, since the cesium coefficient has a high power dependence (probably third) on the phenol concentration. In this test with 1 M OPP in diisopropylbenzene (and in a similar test with 4-chloro-2-phenyl phenol), cesium recovery was >98% from tartrate-complexed simulated Purex waste adjusted to pH ~12.7, with six extraction and two scrub (0.3 M NaOH scrub solution) stages at feed/organic/scrub ratios of 5/5/1. The cesium was completely stripped with a single 0.05-vol contact with 0.05 M HNO_3, yielding a product solution containing 2.4 g of cesium and ~0.07 g of sodium per liter (overall Cs/Na s.f. of ~2×10^4).

In batch extraction tests to determine individual rare earth extraction behavior with D2EHPA in the strontium-mixed rare earth recovery flowsheet, their extraction was somewhat slow (>75% of equilibrium amount in ~1 min) from tartrate-complexed simulated Purex waste, with the order of extraction being Pm > Ce > Eu > Y. By contrast, rare earth extraction from $NaNO_3$-HNO_3 solution (simulated second cycle feed) was rapid and the order was the reverse of that above: Y > Eu > Ce, Pm. In individual

rare earth batch stripping tests with various HNO_3 concentrations, equilibrium was reached rapidly in a noncomplexed aqueous system, and the order of stripping was as expected: Pm, Ce > Eu >> Y.

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