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ABSTRACT

Process development studies are reported on Power Reactor Fuel Processing (Corrosion, Solvent Extraction, Sulfex Process, Uranium Dicarbide Hydrolysis, and Zirflex Process); Fluoride Volatility Processing (Pilot Plant); Radioactive Waste Treatment and Disposal (Engineering, Economics, and Hazards Evaluation, High-activity Waste Calcination, and Low-activity Wastes); Equipment Decontamination; Protactinium Chemistry; Transuranium Elements Studies; Uranium-232 Preparation; and Fission Product Recovery.

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POWER REACTOR FUEL PROCESSING

Corrosion. Aluminum, grade 6061-T6, gained weight when exposed 4-48 hr in refluxing HNO_3-1 M HF when the molarity of the HNO_3 was 14 M or greater. When the molarity of the HNO_3 was decreased or the exposure temperature was lowered, the corrosion rate increased sharply and occurred at the interface or in the solution instead of in the vapor phase. In refluxing HNO_3-1 M HF maximum rates were 85 (vapor), 105 (vapor), 3000 (interface) and 11,500 (solution) mils/mo when the molarity of the nitric acid was 13, 12, 10, and 4 M, respectively. In 14 M HNO_3-1 M HF at room temperature the maximum rate (solution) was 65 mils/mo. In 14 M HNO_3-5 M HF maximum rates (solution) were 4.4 and 294 mils/mo at reflux and room temperature, respectively.

Solvent Extraction. The gross gamma decontamination factor was ~500 when Thorex pilot plant U-233 product, after adjustment to solvent extraction feed conditions, was extracted with either 2.5% TBP in DEB or 2.5% DSBPP in DEB. The extract was scrubbed with 0.8 M $Al(NO_3)_3$, 0.1 N acid deficient. Decontamination during startup was nearly the same as at equilibrium.

Sulfex Process. In 19 Sulfex decladding experiments with type 304 or 316 stainless steel-clad UO_2 pellets, 93-96% of theoretical density, that had been irradiated to levels of 1545 to 28,200 Mwd/t, all specimens were passive in 200% excess of 4 M H_2SO_4. The reaction had to be initiated with iron wire. Losses of uranium and plutonium to the decladding reagent were generally about 0.05%, although in isolated cases they were as high as 0.3%. The decladding solutions, containing up to 10^{10} d/m/ml from activated stainless steel components, required filtration or centrifugation to remove undissolved scale, UO_2 fines, etc.

Uranium Dicarbide Hydrolysis. Hydrolysis of uranium dicarbide ($UC_{1.84}$ with enough free carbon present to make a total C/U ratio of 1.97) in water at 80°C, yielded 44 ml (STP) of gas per gram of carbide consisting of 45% hydrogen, 15% methane, 24% ethane, 9% saturated C_3-C_8 hydrocarbons, 6% olefins, and 0.2% acetylenes. Of the 7.54 mg-atoms of total carbon (0.52 mg-atoms free carbon) present in each gram of the original carbide,

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33% was found in the gas phase, 26% in the wax, and 9% in a water- and ether-insoluble residue; the remaining 31% of the carbon presumably goes to water-soluble compounds which have not yet been isolated. The uranium product is a gray-green insoluble amorphous tetravalent compound which turns black when exposed to air.

Hydrolysis of uranium dicarbide in 6 M H_2SO_4 at 80°C was quite similar to that in water, except that the rate of gas evolution was slower and the uranium product was $U(SO_4)_2 \cdot 4H_2O$, which was insoluble in the sulfuric acid.

Reaction of the dicarbide with 6 N HCl was noticeably different; 56 ml (STP) of gas was produced consisting of 66% hydrogen, 11% methane, 12% ethane, 3% saturated C_2-C_8 hydrocarbons, 6% olefins, and 2% acetylenes. The carbon distribution in the HCl reaction was 25% in the gas phase, 58% in the wax, 8% in a water- and ether-insoluble residue, and 9% unaccounted for. The uranium product was soluble uranous chloride, and the reaction proceeded at about the same rate as the water reaction.

Zirflex Process. Size distribution of PWR UO_2(93-95% density) irradiated to between 9700 and 12,900 Mwd/t averaged 98.9% larger than 10 mesh, 0.4% smaller than 100 mesh, and the remainder between 10 and 100 mesh. Solvent extraction runs with the modified Purex flowsheet confirmed earlier results, giving uranium and plutonium losses to the raffinate between 0.001 and 0.012% and 0.07 and 0.12%, respectively; the addition of sulfuric acid to make the feed 0.1 M in sulfate had essentially no effect on losses to the raffinate. Uranium decontamination factors from β- and γ-emitting contaminants ranged between $2.1\text{-}5.4 \times 10^4$ and 7.1×10^3-1.9×10^4, respectively.

FLUORIDE VOLATILITY PROCESSING

Pilot Plant. Two successful runs were made with >15% burnup, 6.5 year-decayed, zirconium-uranium alloy fuel.

Charges of 48 and 52 kg dissolved at 650-500°C at an HF flow rate of 150 g/min. Dissolution rates in the $NaF\text{-}LiF\text{-}ZrF_4$ salt were 1.8 and 3.1 kg/hr, respectively, based on 90% completion. Corresponding HF

utilization efficiencies were 17.1 and 29.8%. The dissolver off-gas scrubber system performed well with a recycle HF flow rate of ~350 g/min. Uranium was decontaminated from volatile fission products (Ru-106, Sb-125, Nb-95) during dissolution by factors of 2 to > 175. Antimony-125 and Ru-106 were the primary fission products detected in the dissolver off-gas, with only 0.4 and 0.08% of the theoretical feed activity for these two isotopes reaching the off-gas filter in run R-1.

The bulk of the uranium decontamination was obtained in the uranium recovery system (fluorination to UF_6 and sorption-desorption on NaF), with factors of $\sim 10^8$ to 10^9 from Cs-137, Sr-90, and rare earths and of $\sim 10^5$ to 10^7 for Ru-106, Sb-125, and Zr-Nb-95. Specific fission product activities in the UF_6 product were below the analytical limits of detection. Fluorine utilization was low in run R-1 (2.7%), but above average in run R-2 (7.3%). In run R-1, 2.2% of the uranium was transferred to the waste salt because of excessive discharge from the absorber.

The product total cation impurity level in run R-1, < 724 ppm, was slightly lower than the 732 ppm for the TU series (unirradiated fuel), but in R-2 the level was higher, < 874 ppm. However, contaminants in the product for the irradiated fuel runs included plutonium (< 10 ppm), neptunium (< 234 ppm), and technetium (< 69 ppm).

RADIOACTIVE WASTE TREATMENT AND DISPOSAL

Engineering, Economics, and Hazards Evaluation. A cost study of the shipment of calcined solids in 6-, 12-, and 24-in.-dia cylinders was completed. Costs were lowest for shipment in the largest casks considered manageable, which were 60 in. i.d. and contained four 24-in.-dia, nine 12-in.-dia, or thirty-six 6-in.-dia cylinders. Some wastes would have to be aged before shipping to allow decay of generated heat. The longest decay time required was 11 years for acidic Purex waste in 24-in.-dia cylinders.

Weights and costs of casks at minimum ages were about 100 tons and $50,000 for iron casks, 80 tons and $120,000 for lead casks, and 65 tons and $650,000 for depleted-uranium casks. Shipping costs were lowest in all cases for lead casks, and ranged from 0.70×10^{-3} mill/kwh$_e$ for acidic

Purex waste in 24-in.-dia cylinders for a 1000-mile round trip to 32×10^{-3} mill/kwh_e for reacidified Thorex wastes in smaller cylinders for a 3000-mile round trip.

High-activity Waste Calcination. Aluminum borophosphate glasses were prepared which incorporated up to 17% Darex waste oxides, represented volume reductions of 2.5 to 3.2, had bulk densities between 2.44 and 2.74 g/cc, and had initial softening points of 750 to 850°C. Attempts to incorporate 25% Darex waste oxides in similar glasses resulted in products which became devitrified to crystalline or segregated glassy materials.

In a semicontinuous fixation of 28 liters of TBP-25 waste in phosphate-lead glass, ruthenium volatilization was about 16%, but physical entrainment only about 0.1%. Operation with a rising liquid level and a minimum inventory of unmelted solid appears to be advantageous for ruthenium control. A container of a similar glass held at 900°C for 4 weeks slowly developed a vacuum which eventually reached 27 in. H_2O.

Type 304L stainless steel coupled to titanium was corroded at an apparently uniform rate of 77 mils/mo during the final 2 hr (900°C) of a TBP-25 (aluminum nitrate) waste evaporation-glass fixation cycle, compared with an estimated 61 mils/mo when exposed alone. The coupled titanium specimen was corroded at a rate of 31 mils/mo.

In an engineering-scale test with simulated TBP-25 waste, 70% of the mercury in the waste volatilized from the pot calciner during calcination; 20% was removed in a 150°C trap located between the calciner and off-gas condenser, 15% plated out in the 450°C off-gas line, and 30% reported to the condensate.

Chemical and material balance flowsheets were prepared for the pot calciner pilot plant which is to be installed at Hanford. It was demonstrated that the currently designed pots can be satisfactorily sealed by welding. A test rack was designed for testing calciner feed pumps, and a design study indicated the practicability of installing radioactive cell equipment for evaporation-calcination tests in an existing facility originally intended for self-sintering experiments with high-activity wastes.

Low-activity Wastes. In bench-scale equipment, circulation of 5-10% of the clarifier solids to the flash mixer lowered the total hardness (as $CaCO_3$) of the clarifier effluent to 8-14 ppm. Addition of copperas in the flocculator instead of in the flash mixer lowered this to 5.2 ppm.

The presence of 1.7 to 2.4 ppm of Turco 4324 in ORNL tap water had no noticeable effect on the total hardness of the effluent, but 3.2 ppm increased flash mixer and clarifier effluent hardnesses to 44 and 37 ppm, respectively. Operation of this process must be demonstrated on ORNL waste water, which contains 4 to 10 times as much dissolved CO_2, Na^+, Cl^-, F^-, and total solids as tap water and even higher ratios of phosphate.

Vermiculite, used to remove Cs and Sr from the clarifier effluent, performed best at impracticably low flow rates. At 0.25 $ml/cm^2 \cdot min$, 50% Cs breakthrough was reached at 1000 bed volumes although the d.f. from Sr was ~1000 up to 1500 bed volumes. CS-100 resin, on the other hand, gave d.f.'s of 1100 and 1800 for Cs and Sr, respectively, up to 1500 bed volumes at flow rates of 5 $ml/cm^2 \cdot min$.

EQUIPMENT DECONTAMINATION

Development and testing of low-corrosion decontaminating solutions for carbon steel, stainless steel, and aluminum were continued. Although acidic fluoride is an excellent decontaminant for several fission products, plutonium, and americium, its corrosivity to most metals has been a drawback to wide usage. Fluoride was safely added to oxalate-peroxide, however, at increased peroxide concentrations or when aluminum ion was also added. In 0.4 M ammonium oxalate-0.2 M ammonium acetate-0.16 M ammonium citrate-0.05 M fluoride-0.05 M aluminum-0.34 M hydrogen peroxide, with 100 ppm Fe^{3+} added to catalyze H_2O_2 decomposition, carbon steel at 95°C was corroded < 0.001 mil/hr in the first 11.5 hr when the initial pH was 4.0. The rate then rose to 0.15 mil/hr for about 1 hr, after which it dropped to 0.09 mil/hr. The corrosion rate of aluminum in 0.4 M oxalate-0.2 M acetate-0.2 M fluoride-1 M H_2O_2 was 6-9 mils/hr, but the addition of 0.2 M Al^{3+} decreased it to 0.27 mil/hr. In 0.4 M oxalate-0.2 M acetate at 95°C and pH 4.0, carbon steel became passive at about 0.15 M H_2O_2,

but when 0.2 M fluoride was added, 1.1 M H_2O_2 was required for passivity. When 0.2 M Al^{3+} was also added, passivity occurred at 0.38 M H_2O_2.

PROTACTINIUM CHEMISTRY

In fundamental studies on solvent extraction chemistry of protactinium, the relative extractabilities of sulfate and bisulfate from sulfuric acid by N-benzylheptadecylamine were investigated. Potentiometric titration of 1 ml of amine-diethylbenzene, previously equilibrated with aqueous sulfuric acid, in acetone indicated that the amine exists almost entirely as the bisulfate when equilibrated with 10 N sulfuric acid. The bisulfate fraction decreases approximately linearly to 60% as the sulfuric acid concentration decreases to 2 N, and the remainder of the amine is in the sulfate form. The sulfate was determined by titration with KCl solution. In the presence of excess KCl to complex the amine, the first endpoint reached with standard NaOH corresponded to the bisulfate ion and the second to the total amine.

Preliminary experiments on adsorption of Pa-233 from nitric acid solutions on freshly prepared silica gel, commercial silica gel, and unfired vycor glass showed adsorption coefficient maxima, which occurred in 6 to 8 M HNO_3, at 830, 190, and 325, respectively. These results were obtained from 1-hr batch contacts of 20-40 mesh adsorbent with aqueous nitric acid containing ~5 x 10^5 c/m·ml Pa-233.

TRANSURANIUM ELEMENTS STUDIES

The behavior of ruthenium and zirconium in the tertiary amine-lithium chloride system for separating actinides and lanthanides is being studied. Zirconium was quantitatively extracted into 0.6 M Alamine 336 in diethylbenzene diluent from 11 M LiCl. Ruthenium was quantitatively extracted only when H_2O_2 or some other oxidant was present. In stripping with 8-9 M HCl, zirconium distribution coefficients (o/a) were 50 to 200. In stripping with 5-9 M HCl containing H_2O_2, ruthenium distribution coefficients (o/a) were ~100. In the absence of an oxidizing agent, ruthenium was partially stripped. In re-extraction of this ruthenium into fresh solvent

from 5 M HCl containing H_2O_2, ruthenium distribution coefficients were only 5-10. This anomalous behavior of ruthenium may be due to formation of different complexes.

Decontamination factors of an americium solution of > 10^3 were obtained by sorption of these contaminants on Dowex 1 or Permutit SK resin from 5 M LiCl-3 M HCl containing H_2O_2 at 60-80°C.

In a small-scale demonstration run on the proposed ion exchange process for recovering Am-Cm from Pu-processing raffinate, Am-Cm recovery was 99.4%, and cerium, the principal rare earth fission product, was recovered in this product cut. Decontamination factors from Cs, Ru, Zr, and Sb were 500, 20, 100, and 33, respectively. It was estimated that 65% of the Ru, 50% of the Zr, and 40% of the Sb remained on the resin column. The run was made in a shielded cell with 120 ml of plutonium raffinate reading > 100 r/hr. The feed was adjusted to neutral 2.34 M $Al(NO_3)_3$ by evaporation. Americium, curium, and rare earths were sorbed from 15 column displacement volumes onto Dowex 1-10X, 50-100 mesh, resin. The resin column was washed with 5 displacement volumes of 8 M $LiNO_3$, and the product was eluted with 7 displacement volumes of 0.65 M HNO_3.

URANIUM-232 PREPARATION

Four samples of high-purity U-232 were isolated from irradiated Pa-231 by ion exchange. Isotopic analyses of the products, containing 32.9 mg of uranium, showed 98.49-99.66% U-232, 0.0127-0.0311% U-233, 0.0032-0.0109% U-235, and 0.31-1.47% U-238. The principal product contained 21.6 mg of uranium which was 98.90% U-232, 0.0127% U-233, 0.0095% U-235, and 1.075% U-238. In mass-spectrometer analyses, a mass-231 peak was detectable in only one product, indicating < 5% Pa-231 contamination of the uranium.

Protactinium was prepared for reirradiation to produce about 1 g of U-232 by neutralizing the HCl-HF solutions with ammonium hydroxide to precipitate protactinium hydroxide. The precipitate was washed, dried, and calcined at 1000°C. The oxide contained ~44 g of Pa-231 and 9 g of aluminum and was fabricated into six aluminum-jacketed Al-Pa_2O_5 cermet targets which are being irradiated in the ORR. About 13 days will be required to produce the 1 g of U-232.

FISSION PRODUCT RECOVERY

Substituted phenols continued to give good results as extractants for recovery of cesium from Purex waste solutions. A new phenol, 4-sec-butyl-(2-α-methylbenzyl)phenol (BAMBP), extracted cesium much more strongly than any previously tested compound. In a batch countercurrent test with 1 M BAMBP in diisopropylbenzene, 99.9% cesium was recovered from simulated Purex waste (tartrate-complexed and adjusted to pH 12.7) in 5 stages at an organic/aqueous ratio of 1/1. The cesium was 99.8% stripped in a batch contact with 0.05 vol of 0.05 M HNO_3 to give a solution containing 2.4 g of Cs and 0.2 g of Na per liter (overall Cs decontamination from Na by a factor of ~6000). In a test with 1 M o-phenylphenol (OPP) in diisopropylbenzene, > 97% of the cesium was recovered from adjusted simulated Hanford tank farm supernatant at an organic/aqueous ratio of 1/1 in 6 stages. Study of cesium extraction coefficient dependence on phenol concentration showed that it is at least third power. In tests with concentrated basic cesium solutions, maximum organic cesium loading was 1 mole per 6 moles of phenol.

MWG:mrh

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