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ABSTRACT

Process development studies are reported on Power Reactor Fuel Processing (Corrosion Studies, Protactinium Studies, Shear-Leach Process, Uranium Carbides, and Uranium Metal and UO_2 Pellet Dissolution); Thorium Utilization (Fuel Preparation and Pellet Preparation); Radioactive Waste Treatment and Disposal; Equipment Decontamination; Thorium Oxide Studies; Transuranium Element Studies (Process Development and Processing Facility); and Uranium-232 Preparation.

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POWER REACTOR FUEL PROCESSING

Corrosion Studies. Types 347 and 304L stainless steels exposed to refluxing 22 M HNO_3-1 M HF containing 40 g U/liter as $UO_2(NO_3)_2$ and 20 g of solid graphite per liter were corroded at maximum rates of 4.6 and 3.9 mils/mo, respectively.

The corrosion rate of INOR-8 in N_2-CCl_4 increased from 0.7 mil/mo at 485°C to 870 mils/mo at 746°C in 24 hr exposure; that in similar exposures for "A" nickel increased from 1.1 to 1.98 mils/mo in going from a temperature of 480 to 700°C.

In single-cycle 5-hr exposures in O_2 at 765-800°C followed by 5 hr in Cl_2-CCl_4 at 495-500°C, corrosion rates of Haynes 25 varied from 3.1 to 5.2 mils/mo. In similar tests on "A" nickel the maximum corrosion rate was 0.5 mil/mo.

Protactinium Studies. In studies on recovery of protactinium, solutions containing up to 100 ppm Pa-231 in 40 g/liter Th-5 M HNO_3 showed no indication of instability one week after preparation. Batch adsorption experiments showed that the capacity of unfired Vycor glass for protactinium from 6 M HNO_3-0.1 M $Al(NO_3)_3$ is > 360 μg of Pa-231 per gram of glass.

Shear-Leach Process. Particle size measurements on 8.8-kg batches of an ORNL Mark I fuel element (stainless steel-clad UO_2 pellets) sheared into 0.5, 1, and 1.5-in. lengths showed that 84.5, 35.4, and 17.7 wt % of the UO_2 dislodged is < 9520 μ; and 31.9, 11.7, and 6.3 wt % is < 74 μ. Stainless steel and braze metal particles < 2000 μ were 1.6, 0.6, and 0.3 wt % and 0.09, 0.05, and 0.07 wt %, respectively.

Stainless steel-clad UO_2 multitube assemblies sheared to 1-in. lengths were successfully leached. The sheared fuel was fed to the leacher at 1-hr intervals, and visual inspection indicated that uranium leaching was complete after 4 hr. Earlier shakedown runs were unsuccessful owing to solids plugging of the feed lines to the conveyor and leacher during transfer. Acid spray and places for rodding out were placed in the line to eliminate this problem.

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The leach curve relating uranium concentration to time indicated that steady state was approached after 3 hr. The highest uranium concentration of the leachate was 580 g/liter. The overall material balance of the system was within 2%. The uranium inventory as steady state was approached, with a feed rate of 24.6 moles (1 batch) per hour, was equal to about one batch. The composite product and wash water uranium concentrations were 402 and 2.1 g/liter, respectively. Some stainless steel fines were caught in the separators of the leachate and drain liquor streams.

Uranium Carbides. Uranium-carbon alloys containing 1.90 to 2.20 carbon atoms per uranium atom were prepared by arc-melting high-purity uranium metal and spectroscopic-grade carbon. The product had a combined C to U atom ratio of 1.85 ± 0.03 irrespective of the total amount of carbon added to the melt. The excess carbon, beyond $UC_{1.85}$, was present as small flakes of free carbon dispersed throughout the button. Heat-treatment of those specimens with a nominal composition of $UC_{2.00}$ at 2000°C for 6 hr and 1260°C for 238 hr had no effect on the combined C/U ratio. It appears that the maximum amount of carbon that can be reacted with uranium by known techniques is $UC_{1.85}$ and not the stoichiometric $UC_{2.00}$.

Uranium Metal and UO_2 Pellet Dissolution. The instantaneous dissolution rate of uranium metal in boiling 1.5 M $Th(NO_3)_4$-nitric acid increased from 0.31 to 15.9 mg cm^{-2} min^{-1} as the acid concentration increased from 0.05 to 4.2 M HNO_3. The rate was increased further by passing air through the solution during dissolution.

Times for complete dissolution of UO_2 pellets in 10 and 14 M HNO_3 were calculated from instantateous dissolution rates, assuming uniform dissolution of all pellet surfaces, to be 1.5 times the observed times. The actual pellet surface area, recalculated from the observed dissolution rate, increased to a maximum twice the initial area when 35% of the pellet had dissolved.

The dissolution rate of UO_2 pellets did not change appreciably when as much as 0.01 M HF complexed with aluminum (M Al/M F = 3) was added to 2, 6, 10, or 14 M HNO_3.

THORIUM UTILIZATION

Fuel Cycle. The problem of obtaining a uniform uranium distribution in mixed ThO_2-UO_2 prepared by the sol-gel process is being further studied. The tendency for uranium to concentrate in the fine gel particles when sols are evaporated was increased by both incomplete dispersion of the ThO_2 and excess nitric acid in the sol. The optimum NO_3^-/ThO_2 mole ratio for avoiding these conditions was shown by conductimetric titration of ThO_2 with HNO_3 to be dependent on the specific surface area of the ThO_2. For ThO_2 prepared by steam denitration at 475°C, the optimum ratio was 0.08 to 0.09. In four tests the excess uranium in the fine particles, which composed ~3% of the total weight, was decreased from 25 to 2.6% by agitating and digesting ThO_2 in uranyl nitrate solution containing 30% excess nitrate, followed by addition of ammonia equivalent to the excess nitrate.

The use of uranyl nitrate solution obtained by solvent extraction and therefore containing organic impurities gave no operational difficulties and did not affect the final product. Evaporation and steam denitration of thorium nitrate solution in the rotary calciner produced a satisfactorily dispersible ThO_2 product. A 3 mole % uranyl nitrate-97 mole % thorium nitrate mixture was steam denitrated to give a product which was satisfactorily dispersed to a uranium thorium oxide sol.

Pellet Preparation. The addition of 0.13 atom % of carbon, palladium, or chromium to ThO_2 sols in the sol-gel preparation of spheroidal ThO_2 decreased the hourly attrition rate in a standard spouted bed test from 0.36%/hr for pure ThO_2 to < 0.1%/hr. Post-calcination polishing of 1200°C-fired sol-gel ThO_2 pebbles by tumbling with 600 mesh carborundum and then with 4-μ 1200°C-fired ThO_2 decreased attrition rates of ThO_2 spheres by factors of 2.5 to 6.5, to values as low as 0.04%/hr. Approximately 1 kg of thoria and 0.5 kg of 3% U-Th oxide pebbles, ranging in size from 0.15 to 0.21 in. dia, were prepared by the best sol-gel techniques available. Attrition rates of samples in the standard spouted bed test were 0.049%/hr for the 0.2-in.-dia ThO_2 pebbles, 0.03 for the 0.15-in. ThO_2, and 0.02 for the 0.2-in. U-Th oxide.

RADIOACTIVE WASTE TREATMENT AND DISPOSAL

Engineering, Economic, and Hazards Evaluation. The effect of fission product removal on the cost of high-activity waste management was investigated through interim liquid storage, pot calcination, and shipment to salt mines for permanent disposal, and it does not appear that fission product removal will significantly decrease waste management costs. It was assumed that the costs of the separations and handling of the separated fission product concentrates was borne by their sale. The costs of interim liquid storage were decreased about 30% over those of untreated wastes because of decrease in cooling system requirements, but pot calcination costs were unaffected except that all calcinations could be performed immediately in the least expensive 24-in.-dia pots. Shipping costs for the wastes after 90% and 99% fission product removal were about 25% and 50% less, respectively, than for reacidified Purex waste because of thinner shipping cask shielding requirements. Minimum total costs (less costs for disposal in salt) were about 0.141 mill/kwh_e for 99% removal, and 0.147 mill/kwh_e for 90% removal, compared with 0.147 mill/kwh_e for management of acidic Purex waste from which fission products had not been removed.

EQUIPMENT DECONTAMINATION

The fission products, Zr-Nb^{95}, Ce-Pr^{144}, Ba-La^{140}, and Ru-Rh^{106}, which had been baked onto stainless steel at 500°C in O_2-free helium, were removed by decontamination factors of < 5 in 20 min in low-corrosion solutions such as oxalate-peroxide. Such solutions therefore are not adequate for decontaminating such equipment as the stainless steel blowers of the Pebble Bed Reactor. Aluminum decontamination was satisfactory: 10^3 for Zr-Nb^{95} and Ba-La^{140}, and 100 for Ce-Pr^{144} and Ru-Rh^{106}. Carbon steel decontamination was better than that for stainless steel, the d.f.'s in 20 min at 95°C in oxalate-peroxide being 20-40 for Zr-Nb^{95}, 10-38 for Ba-La^{140}, 17 for Ce-Pr^{144}, and 3 for Ru-Rh^{106}. Acetate buffer addition to oxalate-citrate-peroxide made it necessary to use more peroxide in order to keep the solution noncorrosive to carbon steel. An attempt to volatilize Ce^{144} metal from cerium chloride and calcium at 1100°C in helium was unsuccessful.

THORIUM OXIDE STUDIES

A 12 months' irradiation of arc fused thorium oxide, sintered thoria compacts, fired sol-gel material, and a 1600°C-fired thoria powder at full reactor power in the LITR (14 months in the reactor) and a laboratory control experiment was completed. Metallographs of the original arc-fused materials, although the materials are of theoretical density, showed etched pits at former grain boundaries, some cracks, and an occasional large pore. Metallographs of the fired sol-gel material showed a considerable number of micropores and an absence of grain structure. The sol-gel material from the control experiment had a pycnometric density of 10.04 g/cc. The sintered thoria compacts showed a pronounced grain structure, micron-size pores, and, for the materials removed from the control experiment, densities less than theoretical (< 9.83 g/cc for one preparation and 9.62 for a different preparation).

TRANSURANIUM ELEMENT STUDIES

Process Development. In laboratory-scale mixer-settler studies on the Tramex process for actinide purification by tertiary amine extraction from lithium chloride solutions, americium was 99.9% recovered from feed containing 1 mg of irradiated Am-241 (10 watts/liter), with decontamination factors of 5×10^3 from gross γ. Ruthenium and silver were the principal fission product contaminants in the product, Ru^{4+} being extracted with the actinides. In stripping of the actinides with 6-8 M HCl, Ru^{3+}, which forms by slow reduction of the extracted Ru, is also stripped, thus limiting the decontamination from Ru. The use of nitrite to reoxidize the ruthenium resulted in a decontamination factor from Ru of 10^4, but H_2O_2 could not be used since its half-life in 8 M HCl at 60°C is only about 1 min and the solution residence time in the mixer-settler is about 20 min. In a small-scale batch run, separation was more rapid and distribution coefficients were the same as in the experiments with tracer Am-241.

The extraction of barium by 30% Alamine 336 in diethylbenzene from 11 M LiCl solution was increased by the presence of $AlCl_3$. At 0.0025 M

$AlCl_3$ the barium distribution coefficient was 0.1; at 0.06 M $AlCl_3$ it was about 2.

The process will be demonstrated in equipment being installed in cells 3 and 4 of Bldg. 4507. Hastelloy C storage tanks were installed in a pit beneath cell 4. The equipment is designed for remote maintenance by means of especially designed process line disconnects. Contaminated equipment will be renewed and replaced through an air-lock transfer box, now being fabricated, over the top access port of cells 3 and 4. Process equipment, tanks, mixer-settlers, and valves will be constructed largely of Hastelloy C, tantalum, and, where visibility is important, of Homalite plastic. Completion of this installation is scheduled for November of this year.

Processing Facility. The Transuranium Facility for separating and isolating the transuranium isotopes from the target rods irradiated in the High Flux Isotope Reactor will have nine process cells, shielded by 54 in. of magnetite concrete, and eight laboratories. The cells will be served by master-slave manipulators and will have removable top plugs for access. The tops and backs will be served by a bridge crane located in the limited-access area of the building, where shielded space for off-gas filters will also be provided. Four of the cells will contain chemical processing equipment for dissolution, solvent extraction, and precipitation processes; three will contain equipment for remote preparation and inspection of recycle targets; and two will be for remote analytical operations. Preliminary (Title I) engineering of the building structure was completed. Detailed (Title II) design was started, with completion scheduled for Jan. 1, 1963, start of construction for June 1963, and completion of construction for January 1965. With 11 months for installation of equipment and shakedown runs, full-scale operation should start in December 1956. Initial engineering equipment flowsheets were completed, and layout designs of process equipment, cubicle equipment racks, and shielded storage tanks were made. The remote maintenance concept adopted depends on development of remotely operated process line disconnects, and

an initial order for an experimental design that uses investment casting has been placed. Design, development, and fabrication of process equipment were analyzed in detail by the critical path schedule technique, and this detailed arrow diagram was combined with a similar one for construction of the building and shielded cells to form a master schedule. The master diagram was programmed, and the critical path of the project was determined.

The initial installation of the processing facility mockup in Bldg. 9204-1 was completed. The intercell conveyor complex and the associated cubicle port closures are ready for testing, and fabrication of the equipment transfer caisson was started. The feasibility of using a pulsed column as a contactor in separating americium and curium from transcurium elements was partially demonstrated. The flow capacity ranged from 50 to 200 gal hr^{-1} ft^{-2} at 25°C over a pulse frequency range of 80 to 200 cpm for the system: 2-ethylhexylphenylphosphonic acid in diethylbenzene vs 1.5 M HCl, which has a density difference of 0.07 g/cc.

URANIUM-232 PREPARATION

A total of 1.04 g of high-purity U-232 was recovered from the second irradiation of Pa-231. Isotopic analysis of this product showed 99.24% U-232, 0.72% U-233, 0.0014% U-235, and 0.024% U-238. Radiochemical analysis indicated < 0.1% Pa in the uranium product.

The uranium was prepared by irradiating ~45 g Pa-231 to a total nvt of 1.25×10^{20} n/cm^2. The irradiated Pa was allowed to decay 7 days and was then processed through two anion exchange cycles from mixed HCl-HF feed to separate the uranium from protactinium. Tributyl phosphate extraction from 6 M HNO_3 was used for final purification of the uranium. No further preparation of U-232 is planned. After the protactinium has been stored for about one year to allow Pa-233 to decay, it will be purified and returned to the United Kingdom.

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