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ABSTRACT

Process development studies are reported on Power Reactor Fuel Processing (Chop-Leach Process Development, Dissolution Studies on PuO_2 and PuO_2-UO_2, Hydrolysis Studies on Uranium Carbides, Protactinium Adsorption Studies, Solvent Extraction Studies, and Sulfex Hot-Cell Tests); Thorium Utilization Program (Fuel Cycle Development: Fuel Preparation); Waste Disposal Development (Foam Separation Studies); Chemistry Research (Equipment Decontamination, Protactinium Chemistry, and Thorium Oxide Studies); and Transuranium Element Production (Chemical Process Development, Corrosion Studies, Design of Experimental Facilities, HFIR Target Fabrication Development, Process Equipment Development and Transuranium Facility).

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CONTENTS

Page

Abstract . . . . . Cover page

Power Reactor Fuel Processing 5
- Chop-Leach Process Development 5
- Dissolution Studies on PuO_2 and PuO_2-UO_2 5
- Hydrolysis Studies on Uranium Carbides 5
- Protactinium Adsorption Studies 6
- Solvent Extraction Studies 6
- Sulfex Hot-Cell Tests 6

Thorium Utilization Program 7
- Fuel Cycle Development: Fuel Preparation 7

Waste Disposal Development 8
- Foam Separation Studies 8

Chemistry Research 8
- Equipment Decontamination 8
- Protactinium Chemistry 9
- Thorium Oxide Studies 10

Transuranium Element Production 11
- Chemical Process Development 11
- Corrosion Studies 12
- Design of Experimental Facilities 12
- HFIR Target Fabrication Development 12
- Process Equipment Development 13
- Transuranium Facility 13

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POWER REACTOR FUEL PROCESSING

Chop-Leach Process Development. In this process multiple-tube metal-clad oxide fuel elements are sheared into 1/2- to 2-in. lengths and the oxide fuel (UO_2 and ThO_2-UO_2) dissolved in nitric acid. No experimental work was done during this report period because the shear and leach equipment was down for minor repairs and modifications. Further, the data obtained in previous tests are being evaluated to determine the optimum program for the next series of tests.

Dissolution Studies on PuO_2 and PuO_2-UO_2. Since ceramic PuO_2 and PuO_2-UO_2 mixtures are being proposed as reactor fuels, dissolution tests are being made on unirradiated samples of these materials. The instantaneous dissolution rate of PuO_2 pellets having a density of 10.3 g/cm^3 (about 90% of theoretical density) in 7 and 14 M HNO_3 was 3.5×10^{-4} to 5.6×10^{-3} mg cm^{-2} min^{-1}, respectively. The dissolution for PuO_2 in mixtures of 14 M HNO_3, HF, and $Al(NO_3)_3$ (molar ratio, Al/F = 3) increased from 7×10^{-3} to 3×10^{-2} mg cm^{-2}min^{-1} as the fluoride concentration was increased from 0.005 to 0.1 M. The corresponding rate increase in 7 M HNO_3 was 5×10^{-4} to 1.3×10^{-3} mg cm^{-2} min^{-1}.

The dissolution rate of 80% UO_2—20% PuO_2 pellets of density 9.13 g/cm^3 (about 84% of the theoretical density) was 13.5 mg cm^{-2} min^{-1} in 10 M HNO_3—0.5 M HF. After about 2% of the pellet had dissolved, the Pu/U atomic ratio in the solution was found to be the same as that in the pellet, indicating equal dissolution rates.

Hydrolysis Studies on Uranium Carbides. In order to develop a dissolution process for uranium carbide fuels, the basic chemistry of UC_x hydrolysis is being studied. In continuing hydrolysis tests, uranium dicarbide (nominally $UC_{1.91}$; combined C/U ratio, 1.88; single phase at 1000X magnification) yielded 43 ml (STP) of gas per gram of carbide when hydrolyzed in water at temperatures between 25 and 99°C. The off-gas consisted of 48% hydrogen, 10% methane, 26% ethane, 5% C_3- to C_8-saturates, 8% olefins, 1% acetylenes, and 2% unidentified unsaturates. Of the total carbon in the sample, 33% was found in the gas phase and 32% in a water-insoluble wax. Temperature had no effect on the products of the reaction.

This is in marked contrast to work by Litz, who reported 17% hydrogen at 83°C vs 47% at 100°C.

Protactinium Adsorption Studies. In previous studies unfired Vycor glass was evaluated as a selective adsorbent for protactinium in Th-U-Pa fuel solutions. In tests made during this report period, silica gel was evaluated as an alternative adsorbent. Specially prepared silica gel was as effective as unfired Vycor glass powder in removing protactinium from thorium nitrate-nitric acid solutions. One gram of silica gel (20- to 40-mesh) in a column 0.4 cm in diameter and 14 cm long removed 95% of the protactinium from 25 ml of a solution that was 0.5 M in thorium, 11 M in HNO_3, 0.1 M in aluminum, plus a trace of fluoride. The Pa^{231} concentration was about 70 mg/liter. Under similar conditions, 20- to 40-mesh commercial silica gel removed only 57% of the protactinium, and 100-mesh fired Vycor glass powder removed only 13%. Previous experiments had shown that unfired Vycor removed about 96% under similar conditions.

Solvent Extraction Studies. The BNL-Kilorod solvent extraction process for the removal of Th^{228} from U^{233} was modified so that an acid feed may be used. An acid-deficient aluminum nitrate solution was evaluated as a scrubber for the prevention of the extraction of acid with the uranium. The decontamination factor of the U^{233} from Th^{228} and its daughters was about 10^4; the U/NO_3 ratio in the product was 2.18.

Sulfex Hot-Cell Tests. The Sulfex process for the recovery of fuel from stainless-steel-clad UO_2 fuels involves the dissolution of the fuel cladding in sulfuric acid and the subsequent dissolution of the exposed UO_2 in nitric acid. The dissolved UO_2 is then decontaminated by the Purex solvent extraction process. In hot-cell tests, 19 Sulfex decladding experiments were made on type 304 or 316 stainless-steel-clad UO_2 pellets (93 to 96% of theoretical density). The fuel samples had been irradiated to 1545 to 28,200 Mwd/ton. Twenty-one of 32 specimens were initially passive in the 200% excess of 4 M H_2SO_4 used to dissolve the cladding and therefore required initiation of the reaction by wrapping the samples with iron wire. Losses of uranium and plutonium to the decladding reagent ranged from 0.05% to 0.3%. The activity of the decladding solutions was

10^{10} dis min^{-1} ml^{-1} from neutron-activated stainless steel components. The solution was filtered or centrifuged to remove undissolved scale, UO_2 fines, etc. Size distribution of the UO_2 that had been irradiated to between 9700 and 12,900 Mwd/ton averaged 98.9% larger than 10 mesh, 0.7% between 10 and 100 mesh, and 0.4% smaller than 100 mesh.

Solvent extraction runs with the modified Purex flowsheet confirmed earlier results---losses of uranium and plutonium to the raffinate were between 0.001 and 0.012% and 0.07 and 0.12%, respectively. Adjustment of the feed to 0.1 M in sulfate had almost no effect on losses. Uranium decontamination factors for beta and gamma ranged between 2.1 to 5.4 x 10^4 and 7.1 x 10^3 to 1.9 x 10^4, respectively.

THORIUM UTILIZATION PROGRAM

Fuel Cycle Development: Fuel Preparation. In the sol-gel process for the preparation of 3 atom % U-ThO_2 for the Kilorod project, procedures and process-control measures were developed for the preparation of 7-kg batches. Brookhaven National Laboratory specifications for uranium-content uniformity (3 ± 0.03 atom % uranium) were met. Complete dispersion of steam-denitrator-product ThO_2 in uranyl nitrate—HNO_3 solution was consistently demonstrated by the use of a NO_3^-/ThO_2 mole ratio 10% in excess of that shown by conductimetric titration to be optimum for stable 2 to 6 M ThO_2 sols. Dispersion was accomplished by recirculating the hot suspension through a critically safe tank and pipe loop by means of a centrifugal pump. Uniformity of the U/Th atom ratio in all gel fragments was accomplished, and enrichment of the fines with uranium was prevented by neutralizing the excess nitrate with ammonia.

In the calcination of 50- to 200-g batches of 3 atom % U—ThO_2 in a gas-tight furnace, sol-gel oxides calcined in air at 1150°C for 20 min and then reduced and cooled in argon or nitrogen had as low an off-gas content at 1200°C in vacuum (less than 0.005 cc/g) and as high a density as those reduced and cooled in argon—4% hydrogen. In 7-kg charges and a larger furnace, the off-gas content was 10 times higher when no hydrogen

was used, but the increase was thought to be due to the reoxidation of the UO_2 by oxygen that leaked in during cooling.

Thorium oxide—carbon gels were prepared by the sol-gel process, and the carbon was uniformly distributed. Gels in which the C/ThO_2 atom ratio was 5.5 and 4.0 and that were heated to 1800 and 2000°C for 2 hr gave products in which 95 and 80%, respectively, of the oxide was converted to thorium carbide.

WASTE DISPOSAL DEVELOPMENT

Foam Separation Studies. The precipitation of calcium and magnesium from ORNL tap water made 0.005 M each in NaOH and Na_2CO_3 and 2 ppm in Fe^{3+} was tested in 2-, 3-, 4-, and 9-in.-diam sludge columns. With slow (about 10 rpm) rotational agitation of the sludge and at flow rates of 10 to 30 gal ft^{-2} hr^{-1}, hardness was reduced in each column to about 2.6 ppm, as $CaCO_3$, from its initial value of 100 rpm.

In studies of strontium removal by foam separation, wherein decontamination factors of 500 to 5000 were acheived, the feed solution had a composition similar to the effluent from a sludge column, and then a surfactant, dodecylbenzene sulfonate was added. The concentration of the surfactant was 50 ppm.

In continuous, countercurrent foam separation tests, the surfactant was efficiently removed, and its reuse or the avoidance of unnecessary addition of alkylbenzene sulfonates to river water seems workable. The surfactant concentration was easily reduced from 50 to 5 ppm.

CHEMISTRY RESEARCH

Equipment Decontamination. By the use of slightly corrosive solutions, satisfactory decontamination was achieved from fission products that had been baked onto type 347 stainless steel at 500°C in helium. One of the solutions was 0.4 to 0.5 M in oxalic acid and 0.1 M in fluoride ions; the pH was 1.2, and the hydrogen peroxide concentration was maintained at

about 0.015 M by a periodic addition to keep the electrode potential between -50 and -140 mv. The controlled corrosion rate was 0.01 to 0.03 mil/hr. For example, in 1 hr at 95°C, at a corrosion rate of 0.03 mil/hr, decontamination factors were 140 to 200 for Zr-Nb^{95}. When the corrosion rate was 0.01 mil/hr, the DF for Ce-Pr^{144} was 12 in 1 hr, 35 in 2 hr, 124 in 3 hr, and 233 in 4 hr. In the same solution, with the peroxide concentration increased so that the steel became passive and thereby corroded at less than 0.001 mil/hr, decontamination factors were less than 5. A sample from a gas loop (Battelle Memorial Institute) contaminated in helium at 1200°F was decontaminated from mixed fission products by a factor of 41 in 1 hr at 95°C in the solution, with a corrosion rate of 0.01 mil/hr. The final beta-gamma activity was only twice that of background. Samples from the same loop contaminated at 650 and 1000°F had decontamination factors of 125 and 64, respectively, after 1 hr at 95°C in noncorrosive 0.4 M oxalate-0.16 M citrate-0.34 M H_2O_2 at pH 4.0. The DF for the 1200°F sample in the noncorrosive solution was only 2.

Protactinium Chemistry. The distribution coefficients for Pa between aqueous sulfuric acid and diethylbenzene solutions of two secondary amines, S-24 and LA-1, are much smaller than for N-benzyl-heptadecyl amine, but the changes in distribution with amine and sulfuric acid concentration are similar. For all these amines there is a change in the dependence of the distribution coefficient (DC) on sulfuric acid concentration in the range 6 to 9 N, the dependence being higher above this range. For LA-1 and S-24 amines the DC decreases with the fifth power (approximately) of the sulfuric acid concentration in the higher acid range, compared with 8th power (approximately) for N-benzyl-heptadecyl amine. There is good indication that these DC's may be correlated much more simply with the concentration of amine sulfate—$(amine)_2H_2SO_4$—than with the total amine concentration. The amine sulfate concentration is a function of both the amine concentration in the organic phase and the sulfuric acid concentration in the aqueous phase. Since only a small fraction of the amine is in the sulfate form [most is the bisulfate: $(amine)H_2SO_4$] when equilibrated with sulfuric acid in the concentration range of interest, accurate measurements of the amine sulfate concentration are quite difficult. The

titration procedure described previously (ORNL-3321, June 10, 1962, p. 25) has been refined to the point that the limit of detection of amine sulfate is about 1% of the total amine.

The distribution of Pa between aqueous sulfuric acid and Dowex 1 resin was dependent upon the total amount of Pa present. For a given acidity, the amount of Pa remaining in the aqueous phase was constant, and, as more Pa was added, it sorbed on the resin. This concentration in the aqueous phase was directly proportional to the square of the sulfuric acid concentration. Such behavior indicates that the Pa absorbed in the resin has an activity coefficient independent of the concentration.

Thorium Oxide Studies. The thorium oxide preparations irradiated in D_2O (250 to 300°C) in the LITR in experiment C-43-6B were recovered for examination. More than 12 months of irradiation at a neutron flux of 2×10^{13} was achieved. The materials included the P-82 thoria pellets, sintered thoria compacts (prepared by a different method than that for the P-82's), arc-fused thoria pellets, fired sol-gel thoria particles, arc-fused thoria fragments (44 to 74 μ), fired sol-gel thoria spheres (44 to 74 μ), and 1600°C-fired thoria powder (i.e., classified DT-46).

Visual examination of the materials was hampered by the accumulation of a considerable amount of corrosion products. However, the preparations were freed from the bulk of the corrosion products by stirring them in water in a polyethylene beaker with a Teflon-coated stirring bar. Evidently only 13 of the 20 P-82 pellets were submerged in water during the irradiation period and the rest were irradiated in the vapor phase. Those irradiated in water appeared relatively undamaged. The vapor-phase irradiated pellets, however, showed considerable surface damage, and two of the pellets broke during the stirring operation, indicating structural damage. The interior of the broken pellets showed the presence of a tan-colored surface shell and a black coloration from the shell half-way into the center of the pellet. The other sintered-pellet preparation (a portion of which was also irradiated in the vapor phase) showed considerable damage, but the extent was obscured by extensive corrosion product accumulation.

The arc-fused pellets and the fired sol-gel particles appeared virtually undamaged. A fragment knocked from the side of one of the arc-fused pellets during stirring revealed an opaque, glossy-black interior. Before irradiation the arc-fused pellets were light-red and translucent.

The ground arc-fused material appeared visibly unchanged, while the Houdry spheres had absorbed corrosion products and showed some loose agglomeration. The DT-46 material had escaped from its stainless steel container around the fritted disc that formed the enclosure and then had settled on the lower container. It had been formed into a porous plug (readily broken in two) that contained about 2% iron, nickel, and chromium.

Detailed examination of the materials is under way. Material-recovery balances will be obtained and preparations were made in order to obtain wear tests, metallographic cross sections, and x-ray diffraction patterns of the surfaces and interiors.

TRANSURANIUM ELEMENT PRODUCTION

Chemical Process Development. In solvent extraction tests with short-cooled materials, it was found that short lived Ag^{111} and Tc^{99} followed the transuranium elements in the Tramex process. Te^{132} appeared to partially extract and a small fraction followed the products. Mo^{99}, I^{131}, and I^{132} were extracted but did not strip.

The effect of alpha radiation on the amine solvent used in the Tramex process was studied in a batch test with Cm^{242}. At a level of 3 w/liter a slight decrease in curium distribution coefficient, from 3.6 to 3.2, was noted at 60 whr/liter. Lanthanide distribution coefficients remained less than 0.1. After 200 whr/liter some interfacial material formed, but no difficulty in phase disengagement was noted throughout the experiment, which was terminated at 300 whr/liter. The extracted Cm^{242} was readily stripped with 9 M HCl after this extreme exposure.

Nickel from corrosion or target material follows the transplutonic elements through the Tramex process. However, tests indicated that the nickel can be separated from the product by an oxalate precipitation.

In a solution that was about 0.1 M in HNO_3 and in the presence of ammonium ion, a separation factor of 250 was obtained when the transplutonic elements were precipitated as oxalates.

Corrosion Studies. The Tramex process involves handling both neutral and HCl-acidified LiCl solutions over a range of temperatures from about 40°C to the boiling point. At the higher temperatures only tantalum and Zircaloy-2 have been found to be satisfactorily corrosion resistant. Hastelloy-C can be used for applications at lower temperatures.

The possibility of hydrogen pickup in tantalum and Zircaloy-2 was examined in a number of environments in 1000-hr tests. No hydrogen pickup was detected in tantalum exposed in the solution and vapor of a 10 M LiCl—0.1 M HCl mixture at about 135°C. Similarly, no pickup was found at 35°C in a 10 M HCl—0.0023 M $LaCl_3$ solution that contained H_2O_2. However, tantalum plate on stainless steel base metal was severely embrittled during 300 hr in oxygenated and boiling 6 M HCl solution when the base metal was attacked through defects in the planting. A solution-exposed Zircaloy-2 specimen exhibited some evidence of hydrogen pickup after 1000 hr at 35°C in a 10 M HCl—0.0023 M $LaCl_3$ solution that contained H_2O_2. The hydrogen content of the specimen was 120 ppm, compared with 65 in the unexposed material. No hydrogen pickup occurred in the vapor-exposed specimen.

Design of Experimental Facilities. Equipment for testing the complete Tramex process at full activity level and on a pilot scale is being installed in cell 4, Building 4507. Design of this facility is 85% complete, and the piping drawings are complete. Installation of two 200-liter storage tanks with their shielding was completed, and the interior of the cell was painted. The panel board is 90% complete, and the transmitter rack is being installed. Completion of this installation is scheduled for February 1, 1963.

HFIR Target Fabrication Development. The HFIR irradiation targets will consist of cermet pellets of aluminum powder and transuranium-element oxides enclosed in aluminum tubes. In simulated pellets made from -100 mesh aluminum and UO_2 powders, the aluminum was the continuous

phase, as confirmed by metallography. In previous tests with aluminum and Gd_2O_3 powders which had been blended in a rod mill, the oxide was the continuous phase, and thermal conductivity was only about 20% as high as that for aluminum. This was attributed to the very small particle size of the Gd_2O_3 after the milling step.

The welding conditions required for producing good welds on the end caps were: a current of 38 to 40 amp and a tube rotational speed of 9 to 10 rpm. With the plug joint design used, this gave a satisfactory 70% penetration. Difficulty was encountered, however, in tack welding the hexagonal spacer tube that surrounds each target and mechanically aligns the individual targets in the target assembly. When three full-scale tubes were hydrostatically collapsed onto the pellets, about half of the spacer-tube tack welds were sheared.

In a set of experiments to determine the optimum pressure of the tube collapse, it was found that collapse is very nearly complete at 8000 psi, but, somewhat higher pressure will be needed to provide the required intimate contact required for good heat transfer.

Process Equipment Development. After minor modifications the conveyor automatic port closure was operated through 1000 cycles without difficulty and with little wear. The intercell pass-through was tested and modifications recommended. An electric impact wrench with torque-limiting socket-wrench extensions was tested and recommended for use with manipulators in order to prevent bolt shearing or thread damage.

Four protective coatings withstood 3.4×10^9 r of exposure from a Co^{60} source while submerged in deionized water, and the recommended coating, from results to date, is the Amercoat No. 74 surface with Fiberglas and No. 66 Seal epoxy system.

Transuranium Facility. The architect-engineer design is about 75% complete and is progressing on schedule. Completion is expected by December 15, 1962. Seventy-two drawings and 38 specification sections have been received for ORNL review. Detail drawings of the intercell-conveyor housing were completed and transmitted to the architect-engineer for inclusion in the contract package. The housing to be installed by

the lump-sum contractor will be provided by ORNL. The facsimile of the equipment-transfer system is progressing. The hoist and door lock are being constructed. Drawings of the top assembly are complete and have been issued, as have the drawings of the bottom assembly. The installation and assembly drawings for the cell cubicle were completed, and component drawings for the architect-engineer design package were revised and transmitted.

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