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CHEMICAL TECHNOLOGY DIVISION MONTHLY REPORT FOR APRIL 1963

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ABSTRACT

Process development studies are reported on Power Reactor Fuel Processing (Hydrolysis of Thorium Carbides, Extraction of Protactinium from Nitric Acid-Hydrofluoric Acid Solution, Protactinium Adsorption Studies); Thorium Utilization Program (Fuel Cycle Development: Fuel Preparation); Waste Disposal Development (Foam Separation Studies); Chemistry Research (Equipment Decontamination and Thorium Oxide Studies); Transuranium Element Production (Chemical Process Development); and Isotope Development Program (Recovery of Fission Products and Cm^{242} Preparation).

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POWER REACTOR FUEL PROCESSING

Hydrolysis of Thorium Carbides. -- The amount of uranium in uranium carbides is readily determined gravimetrically by burning the specimen in oxygen at 950°C, cooling, and weighing the residual U_3O_8; unfortunately this procedure is not satisfactory for thorium carbides. The finely divided ThO_2, even after heating at 1250°C, gains weight upon cooling through surface sorption, resulting in a significant error (about 2%) in the thorium analysis. This difficulty has been overcome by burning weighed samples in a thermobalance and determining the weight of the ThO_2 at 950°C.

The ignition temperature in oxygen for thorium dicarbide is about 540°C, and for thorium monocarbide about 630°C. At 650°C, 95% of the thorium dicarbide reacted within 30 min, whereas after 3 hr only 85% of the monocarbide reacted. Both samples were -10 +50 mesh. The use of particles larger than 10 mesh is not recommended for analytical purposes, since the ThO_2 product tends to form a protective barrier that hinders further oxidation.

Extraction of Protactinium from Nitric Acid-Hydrofluoric Acid Solution. -- Multiple extraction and Martin-technique experiments, using tracer Pa^{233}, have demonstrated that essentially all the protactinium in 5 M HNO_3 is extractable in 30% tributyl phosphate in n-dodecane. The protactinium distribution coefficient is about 4. When 0.02 M HF was added to the 5 M HNO_3, about 94% of the protactinium became unextractable, and the distribution coefficient of the extractable species was reduced to about 0.07, indicating that almost all of the protactinium was complexed by fluoride.

Protactinium Adsorption Studies. -- The adsorption coefficient of unfired Vycor for protactinium adsorption from 10 M HNO_3 was decreased by factors of 10, 100, and 1000, respectively, when 0.01, 0.02, and 0.03 M HF was present. About 7-1/2 moles of aluminum per mole of fluoride were required to completely complex the fluoride in solutions containing 0.04 M HF, so that the distribution coefficient was not affected. The distribution coefficient was approximately 1400 after a 24-hr batch equilibration between 10 M HNO_3, about 6 g of thorium per liter , 1.7×10^6 counts of Pa^{233} per minute per milliliter, fluoride, and 20 g of 60-80 mesh unfired Vycor per liter. With feed solutions containing 112 g of thorium per liter, the coefficient decreased from 1200 with no fluoride present, to 345 when the fluoride concentration was 0.04 M. The presence of 7-1/2 moles of aluminum per mole of fluoride increased the coefficient to about 800.

THORIUM UTILIZATION PROGRAM

Fuel Cycle Development: Fuel Preparation. -- In studies of the kinetics of the carburization of thoria and of 5 mole % uranium-thorium oxide, where the reactant mixtures were prepared by the sol-gel process, reaction rate constants were increased tenfold by a 100°C temperature rise in the 1500 to 1700°C range. Increasing the C/metal mole ratio of the reactants from 4.3 to 5.1 doubled the reaction rates for corresponding temperatures, but a further increase in ratio produced no further effect on rates. When uranium was also present, corresponding rates to those for thoria alone were achieved at about 100°C lower. Carburizations were greater than 99% complete in 4 hr of heating time at 1500 to 1600°C when 5 mole % uranium was present.

Conductimetric titration of the system thorium oxide-carbon-water showed a critical nitrate demand similar to that for the system thoria-water for complete dispersion to stable sols. Gels obtained by evaporation of these sols were maximally reactive during carburization.

The size of spherical particles produced by spraying the sol into stirred carbon tetrachloride can be controlled by varying the velocity of the tips of the agitator blade. A modified Reynolds number of the agitator tips with respect to carbon tetrachloride of 17,000 gave particles having a geometric mean size of 194 μ, with a standard deviation of 1.5. The feasibility of re-solling off-size gel particles was established.

Addition by spray of 10% by weight of water to a 3 mole % uranium-thorium oxide gel that had been dried at 135°C shattered the dried gel and produced a coarse- and medium-range particle size. Ballmilling the same type of gel for 1 hr produced particles more than 95% of which

were -200 U.S. mesh size. Calcining a mixture of 75 wt % shattered and 25 wt % ballmilled gel by the sol-gel procedure produced an oxide mixture that was easily vibrated to 86% of theoretical density, which is satisfactory.

Twenty-seven stainless steel irradiation-test capsules containing sol-gel uranium-thorium oxide or plutonium-thorium oxide have been or are being irradiated at burnups of 5,000 to 110,000 Mwd/metric ton uranium + thorium. Other irradiation conditions include linear heat ratings of 25,000 to 60,000 Btu/hr-ft, center-line temperatures up to 4000°F, and clad temperatures to 1300°F. Seventeen specimens removed from the reactor were examined. Accumulated data indicate that the sol-gel oxide is potentially a satisfactory fuel, with a thermal conductivity of about that of UO_2 at corresponding temperatures.

WASTE DISPOSAL DEVELOPMENT

Foam Separation Studies. -- The composite laboratory unit, consisting of a 3-in.-diam sludge column to precipitate most of the calcium and a 1.5-in.-diam foam column to remove strontium, was operated with tap water spiked with Sr^{85} tracer. The flow rate was 20 gal ft^{-2} hr^{-1} in the sludge column and 60 gal ft^{-2} hr^{-1} in the foam column. Calcium and magnesium precipitation were induced by making the water 0.005 M each in Na_2CO_3 and NaOH, while coagulation was aided by the addition of about 4 ppm of Fe^{3+}. Gas-to-liquid flow ratios in the foam column were 10 to 15. Strontium decontamination factors were 10^3 to 10^4, without filtration of the decontaminated water.

Engineering studies were continued in 6-in. and 24-in.-diam foam separation columns, using dodecylbenzenesulfonate as the surfactant. The 24-in.-diam foam column with feed introduced through 19 tubes in a 5-in. triangular spacing was operated at varying flow rates, and the channeling below the feed tubes was observed visually. Channeling was visible 18 to 30 in. below the tube ends for 40 gal ft^{-2} hr^{-1}, and 10 to 22 in. for 15 gal ft^{-2} hr^{-1} liquid feed rates. When 20-mesh screens were used across the column cross sections in an attempt to distribute the liquid uniformly and thus reduce channeling, liquid accumulated on the screens and "dumped" through at short intervals to give very severe channeling. The capacities of air-operated sonic whistles as foam breakers were 0.05 to 0.10 ft^3 foam per standard cubic foot of operating air; these capacities were significantly reduced by thin, 0.001 to 0.002 in., rubber or aluminum membranes between the whistle and the foam. The concentrations for a continuous three-stage surfactant recovery system test agreed

with calculated values for a surfactant distribution coefficient of 7×10^{-4} cm.

CHEMISTRY RESEARCH

Equipment Decontamination. -- Satisfactory low corrosion type of decontaminants were developed for stainless steels that had been contaminated from the gas phase at 650°C with mixed fission products, and for stainless steels contaminated by aqueous solutions and then baked in helium at about 500°C.

The most effective solutions were mixtures of 0.5 M oxalic acid with 0.1 M fluoride, made either slightly corrosive (0.02 mil/hr) with 0.015 M hydrogen peroxide or made nearly noncorrosive (0.003 to 0.005 mil/hr) with 0.1 to 1 M peroxide, and used at 95 ± 3°C. The slightly corrosive solution dissolved thin, black oxide coatings formed on stainless steels heated to 500 to 650°C in the presence of a trace of air. For this reason it is more effective as a decontaminant for steel than the noncorrosive solution . For example, a piece of type 304 stainless steel tubing contaminated at 650°C in a helium gas loop at Battelle Memorial Institute was decontaminated from mixed fission products by a factor of 41 (to only twice background level) by immersion in the slightly corrosive solution at 95°C for 1 hr. The decontamination factor in noncorrosive oxalate-citrate-peroxide solution at pH 4 and 95°C (a solution used for carbon steel decontamination) was only 2. Other contaminated samples from the same loop, but from cooler areas (340 and 540°C), were decontaminated in the pH-4 solution by factors of 125 and 64, however.

Decontamination factors for aqueous-contaminated and helium-baked (500°C) stainless steel coupons, when treated with the fluoride-containing solutions for 2 to 4 hr at 95°C, were 100 to 200 for $Zr\text{-}Nb^{95}$, 200 to 300 for $Ce\text{-}Pr^{144}$, 70 for $Ru\text{-}Rh^{106}$, and 70 for $Ba\text{-}La^{140}$.

Stainless steel pipe contaminated in the Metals and Ceramics Division by exposure to helium flowing over heated neutron-irradiated UC_2 was easily decontaminated by suitable oxalate-peroxide reagents. Iodine and tellurium deposits collected below about 300°C responded well to the pH-4 solution, and those collected above this temperature were dissolved by the oxalic acid-peroxide-fluoride solutions.

Thorium Oxide Studies. -- X-ray and metallographic examination of the thoria preparations (P-82 pellets, arc-fused pellets, and sol-gel fragments) irradiated wet (250 to 300°C) and dry (estimated maximum temperature less than 300°C) in the LITR to exposures of 2.5×10^{18} fissions per gram were completed (TM-409 and -444). Relatively little change occurred as a result of the irradiation, indicative of the marked resistance of cubic structures to radiation damage. The material irradiated under D_2O showed a slight lattice expansion (less than 0.5%), while that irradiated dry appeared relatively unaffected. Apparent crystallite sizes for the irradiated P-82 and sol-gel materials ranged from 950 to 2000 A, compared with original crystallite sizes uniformly greater than 2000 A. Hence there may have been some slight crystallite damage. Diffraction patterns of the irradiated arc-fused pellets, which were originally monocrystalline, indicated that no extensive formation of large angle boundaries occurred in the pellets as a result of the irradiation.

Metallographs of the irradiated samples resembled those of the original materials. The polished and etched sections of the P-82 pellets showed grain sizes similar to those of the unirradiated pellets. Neither the irradiated nor unirradiated arc-fused and sol-gel-prepared materials showed a grain structure after polishing and etching.

TRANSURANIUM ELEMENT PRODUCTION

Chemical Process Development. -- All chemistry concerned with processes needed for producing the transuranium elements is included in this program. Tramex process development is discussed as part of Cm^{242} preparation in this report. Other studies include: the effect of solvent diluent in the phosphonate process, the separation of actinides and lanthanides in carbonate solutions, methods of preparing PuO_2 for HFIR targets, and the determination of the californium content of irradiated TRU plutonium-aluminum alloy rods.

Solvent diluent has an important effect on the phosphonate process for splitting transplutonium elements into an americium-curium and a transcurium fraction. A correlation has been noted between the dielectric constant of the solvent used to dilute 2-ethylhexylphenylphosphonic acid [2-EH(ØP)A] and distribution coefficients of americium and californium between 1 M 2-EH(ØP)A and 1 M HCl. The californium distribution coefficient decreased from 45 for heptane diluent, with a dielectric constant of 1.9, to 3 for toluene diluent with a dielectric constant of 2.4. Americium distribution coefficients with these two diluents were 0.37 and 0.028, respectively.

Methods of separating actinides and lanthanides in carbonate solutions are being investigated. If satisfactory methods can be found to replace methods using chloride systems, corrosion problems will be greatly reduced. Scouting tests indicate that it may be possible to separate americium and curium from most lanthanides by either extracting the lanthanides into quaternary amines or loading them on strong-base anion exchange resin from dilute carbonate solutions. The group separation of actinides

and lanthanides does not appear possible because the heavier actinides have greater distribution coefficients than the lighter lanthanides. Distribution coefficients between 30% Aliquat 336 in diethylbenzene and 0.5 M $NaHCO_3$ were as follows: Am, 0.52; Cm, 0.65; Cf, 2.03; Es, 2.51; Ce, 1.0; and Eu, 4.8. The practical application of this method is limited by the solubilities of actinides and lanthanides in the dilute carbonate solutions. Solubilities have not been determined but they are probably very low.

A method was investigated for preparing dense, coarse particles of PuO_2 for use in HFIR target prototypes.

A solution of 0.5 M $Pu(NO_3)_4$ in 4 M HNO_3 was rapidly mixed with an equal volume of 8 M NH_4OH to precipitate $Pu(OH)_4$. The precipitate was washed thoroughly with 2 M NH_4OH and dried at 150°C. The dried solid was fired in air at 1200°C to produce a glassy solid with a density of 10.99 (96% theoretical). Since most of the particles were from 1 to 3 mm in diameter, this method, followed by careful grinding and screening, appears to be satisfactory. When PuO_2 particles less than 10 μ in diameter are mixed with -325 mesh aluminum powder and pressed into cermets, the oxide phase is continuous, and the thermal conductivity of the pellet is low. With PuO_2 particles ranging from 20 to 200 μ, the aluminum phase will be continuous, and conductivity will be satisfactory for irradiation in high neutron fluxes.

A nitric acid solution of eight plutonium-aluminum alloy rods, irradiated for the transuranium element program, was analyzed for californium; two anion exchange cycles from chloride solution were used to isolate the transplutonium elements, and chromatographic elution from

cation exchange resin with α-hydroxyisobutyrate solution was used to separate the californium. The californium was analyzed by both alpha pulse and fission counting. The fraction of transplutonium alpha counts due to Cf^{252} were 3×10^{-7} and 6×10^{-7} for duplicate determinations. The difference in these two values probably indicates the accuracy of the determinations. Based on these numbers, the eight Pu-Al alloy rods contained between 0.45 and 0.90 μg of californium. The balance of the TRU rods (which have been irradiated longer) should contain 100 to 150 μg of californium.

ISOTOPE DEVELOPMENT PROGRAM

Recovery of Fission Products. -- In extractions of strontium from 3 M $NaNO_3$ solution with 0.3 M Sunaptic Acid A (a commerical naphthenic acid) in Amsco 125-82, the extraction coefficient increased to about 70 with increase in pH to 7.5 and then decreased rapidly with further increase in pH. Maximum coefficients were much lower (2 to 6) in extractions from citrate-complexed simulated formaldehyde-treated Purex waste (FTW). In the latter tests, strontium coefficients were about threefold higher when pH adjustment was made during rather than before extraction. The strontium/sodium separation factor in the tests with FTW solution ranged from 60 to 150.

In a batch countercurrent test using two extraction stages and one water-scrub stage, 94% of the iron was extracted from simulated formaldehyde-treated Purex waste (FTW) with 0.24 M Primene JM in Asmco 125-83 while extracting only about 5% of the cerium. Greater than 98% of the cerium was then extracted by contacting the raffinate with six successive volumes of the same solvent at an aqueous/organic ratio of 10/1.

Cm^{242} Preparation. -- Details of the Tramex process are being studied to ensure successful operation for Cm^{242} isolation from irradiated AmO_2-aluminum cermets.

The principal effect of alpha radiation in Tramex feed is a loss of acid. Acid-depletion G values (G_{-H^+}) were determined for synthetic feeds of 10 M LiCl containing 2.5 and 15 w of Cm^{242} per liter. Previously reported G_{-H^+} values of 4.0 and 5.6 were averages for a wide range of acid concentration. Recent data show that G_{-H^+} values are dependent upon acid concentration. Over the range 0.4 to 1.0 M HCl, G_{-H^+} values

of 10 to 20 were measured. At lower acidities, G_{-H^+} values were 2.2 at 2.5 w/liter and 1.0 at 15 w/liter. If G_{-H^+} is slightly greater than 1 at 10 w/liter, which is the proposed operating level, acid will be lost at the rate of 0.1 mole per liter per day. Since acid concentration must be held between 0.01 and 0.1 M in order to obtain both a stable feed and sufficient extractability of the transplutonium elements, acid loss by radiolysis means that adjusted feeds may be stable for less than a day unless acid is replenished. Acid can be replenished by HCl gas bubbled through the feed; however, the equilibrium acidities of 1.35 M at 60°C and 0.4 M at 120°C for HCl gas at 1 atm are too high for satisfactory extraction.

Careful investigation of the effect of $AlCl_3$, LiCl, and HCl concentrations in Tramex feed on americium distribution coefficients is in progress. Concentrations must be carefully controlled for the Tramex process to work satisfactorily. For example, the americium distribution coefficient between 0.6 M Alamine 336·HCl--diethylbenzene and 10 M LiCl--0.1 M $AlCl_3$--0.02 M HCl is 4.0 but is decreased to 1.0 by either increasing the acid to 0.14 M or decreasing the $AlCl_3$-plus-LiCl salt concentration to 9.5 N.

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