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F. L. Culler, Jr.

ABSTRACT

Process development studies are reported on Power Reactor Fuel Processing (PuO_2 Pellet Dissolution, Chloride Volatility--Solvent Extraction of HTGR Fuel, Physical Properties of $ThOCl_2$--Aseotropic HCl Solutions, Flowsheet Development of UC Fuel, Solvent Extraction Studies, Shear and Leach Studies, Fluoride Volatility Processing: Aluminum Alloy Flowsheet Development, Fluoride Volatility Processing: Retention of TeF_6, and Fluoride Volatility Pilot Plant) and Chemistry Research (Chemical Applications of Nuclear Explosions, Ion Exchange Studies, Mechanisms of Separations Processes, Solvent Extraction Research, Process Chemistry of U and Th, Solvent Extraction Studies, and Volatility Studies).

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POWER REACTOR FUEL PROCESSING

Chloride Volatility Corrosion Studies. -- Welded specimens of "A" nickel and Haynes 25 corroded at rates of 27.3 and 40.4 mils/month, respectively, when exposed to a cycle consisting of 5 hr in Cl_2-CCl_4 at 500°C followed by 5 hr in oxygen at 1000°C. "A" nickel, Nichrome V, and Haynes 25 corroded at respective rates of 1.2 mils/month (19 cycles), 2.0 mils/month (18 cycles) and 29.6 mils/month (7 cycles) in cyclic oxidation-chlorination tests. The cycles consisted of oxidation of wet graphite fuel in oxygen at 800°C for 5 hr, followed by chlorination in chlorine at 500°C for 5 hr.

Hastelloy B corroded at rates of 0.5 and 1.5 mils/month for 840-hr exposure in vapor and solution phases, respectively, of boiling 3 M $ZrOCl_2$--3 M HCl.

Hydrolysis of Uranium Carbide. -- The general study of the hydrolysis of carbides in acid and basic aqueous solutions was continued. The volume of gaseous products obtained from the reaction of uranium monocarbide with various concentrations of caustic increased from 103 ml/g (STP) with 2.0 M NaOH to 115 ml/g with 18.6 M NaOH. The gaseous products from 2, 4, and 6 M NaOH consisted of about 26 vol % H_2 and 72 vol % CH_4. With 8.9 M NaOH, the percentage of hydrogen increased to 32 vol %, while the CH_4 decreased to 65 vol %. With 12.2 and 18.6 M NaOH, the gaseous products consisted of 35 vol % H_2 and 61 vol % CH_4. In contrast, the gas obtained by the reaction of uranium carbide with water contained 13 vol % H_2 and 84 vol % CH_4. About 92% of the carbon originally present in the uranium monocarbide was found in the gas phase and 0.5% in the sodium hydroxide-insoluble solids. The time for 95% of the carbide to react

varied from 2.5 hr with water to 6 hr with 2 M NaOH and 41 hr with 18.6 M NaOH.

THORIUM UTILIZATION PROGRAM

Fuel Cycle Development: Fuel Preparation. -- The reaction of ThO_2 with carbon to form ThC and ThC_2 was found to be first order with respect to ThO_2. In the presence of carbon in excess of that necessary to form ThC_2, the apparent activation energy is 112 kcal, and a rapid and controllable reaction that is apparently independent of C/Th atom ratio between 4.3 and 6.8 and U/Th atom ratio of 0 to 0.05 is obtained. When the C/Th atom ratio for the reactants is less than 4, a principal reaction product is thorium monocarbide, with negligible unreacted ThO_2. The activation energy is about 104 kcal. The bulk density of the product varies from 2.74 to 8.58 g/cc. Free carbon contents vary from 2 to 22%.

Sols of 3%-uranium--97%-thorium oxide are being dried in an oven at 135 to 150°C. The drying temperature used previously was 80°C. The higher temperatures shorten the drying cycle without affecting the density of the gel product. The gel products when fractured by ball milling for about 2 hr and fired at 1150°C give a fired oxide whose particle size distribution is suitable for vibratory compaction without further sizing.

Thoria gel spheroids are being prepared by dispersing ThO_2 sols to droplets in carbon tetrachloride-isopropyl alcohol and "setting" them by extraction of water from the droplets. In initial studies, spheres were formed by spraying sol through an orifice into CCl_4 and isopropyl alcohol. Attempts to duplicate these results gave teardrop, pear, egg, and disk shapes. Satisfactory spheroid particles are now being produced by agitation of the sol with the CCl_4--15 to 45% isopropyl alcohol to which 0.1 to 0.3 vol % of Span-80 (sorbital monoleate) has been added.

Kilorod Program: Purification of Uranium-233 Nitrate Solution. -- Three solvent extraction runs were conducted to purify about thirteen kilograms of uranium-233 as nitrate solution for subsequent sol-gel treatment, and to demonstrate the operability of a chemical and equipment flowsheet for uranium-233 purification. The mechanical performance of the equipment was without incident.

A compound extraction-scrubbing column is used to selectively extract and scrub the uranium from a highly salted feed (5 mg/ml U, 220 mg/ml Th, 2.4 M HNO_3). A solvent containing 2.5 volume percent di-sec-butylphenylphosphate in di-ethylbenzene is used for extraction and the scrub solution is 0.8 M Al and 0.4 M acid deficient.

The uranyl nitrate product solution met all specifications required by the sol-gel process.

The results tabulated below reflect the pilot plant experience to date with the solvent extraction process for uranium-233 purification.

Uranium-233 Purification by Solvent Extraction - Pilot Plant Results

Uranium-233 purified as UNH 125 ± 25 mg/ml		13,400 g
NO_3/U mole ratio in U-233 product solution		2.2 to 2.4
Recovery of uranium-233-per cent of amount treated		99.6 to 99.8
Decontamination factors - product content relative to amount in feed:		
Thorium	3000 to 4600	
Gross γ	230 to 416	
Radium-224	$> 5 \times 10^3$	
Thorium content in uranium-233 product - $\frac{Th}{Th + U}$		1.2 to 3.0 w/o
Aluminum content in uranium-233 product - ppm of U		40 to 140
Nitric acid content of uranyl nitrate product solution M		0.06 to 0.12

Uranium recovery was limited to 99.8 per cent because the 20-ft tall stripping column provided only 1.2 to 1.4 stages for stripping the uranium from the loaded solvent. This spent solvent was continuously recycled to the bottom of the extraction column and consequently allowed a high uranium loss to the extraction waste stream. With three stripping stages, the uranium recovery would be 99.95 per cent.

The aluminum (100 ppm of U) and thorium (3 w/o) content of the purified uranium-233 product are satisfactory for sol-gel process use.

Sol-Gel Preparation of Uranium-233 Thorium Oxide. A total of 200 kg of fired (1150°C) 3% uranium-233 oxide - 97% thorium oxide product meeting chemical specifications for the process has been prepared.

Cold tests were made, with depleted uranium solution and thorium oxide powder produced locally from thorium nitrate, to establish operating conditions and operational procedures and to test the equipment. Premature failures of the furnace heating elements were corrected by the relocation of thermocouples and the re-routing of purge gas flow through the furnace oven cavity. Initially the tray dryer had insufficient heat transfer capacity, and additional steam coils were installed in the dryer oven cavity.

Since the beginning of sol-gel processing with purified uranium-233, the preparation of oxide has become almost routine operation. These operations involve blending of uranium-233 nitrate solution with thorium oxide powder to produce the sol; subsequent drying of the sol at 80°C; and, firing of the dry gel at 1150°C for 4 hr under reducing atmosphere. Difficulties in obtaining the desired 3.0 ± 0.03 per cent by weight U-233 in the uranium-thorium mixture were mainly the result of inaccurate

determination of the uranium content in the feed solution. A separate uranium nitrate feed storage tank, 5-in. ID by 20-ft. tall, was installed to replace the glass Raschig ring packed tank previously in use. The metal ratio ($\frac{U}{U + Th}$) has been held to 3.00 ± 0.03 per cent (Spec., 3.00 ± 0.05) since this equipment change. Experience to date has shown the variation in the uranium content to be about ± 1% when determined by the coulometric procedure.

One of the major objectives of this facility is to obtain radiation data for the handling of U^{233}, on a plant scale. This U^{233} handled contains 37-40 ppm U^{232} from which several hard-gamma daughter products are generated. The average radiation exposure to personnel throughout the high level phase of the program has been 17 mrem/man-week. A maximum single exposure of 50 mrem was experienced during a 4-hr period while repairing the ball mill.

While the radiation levels in Kilorod have been in good agreement with those anticipated, decontamination data has been obtained that will permit a more accurate prediction of radiation levels in future installations. Some interesting observations have been made, noticeably in the calcination step. A loss of Rn^{220} and Ra^{224} has been noticed in this operation, which results in a lower than anticipated radiation at longer postpurification times.

Rod Fabrication.* Work was continued in the rod fabrication housed in cubicles on the first and second level of cell 4 building 3019. This facility receives fired 3 wt % uranium-233 oxide in thorium oxide which is prepared on the third level of cell 4 in the sol-gel facility.

A total of 89 rods meeting specifications have been produced from 100 kilograms of feed oxide. Seventeen rods were rejected because of

*Under direction of Metals and Ceramics Division.

density variations along the length of the rod greater than the ±2% allowed. The rejection rate experienced to date is about 20 per cent of the total rods fabricated. Rejected rods are dismantled and the oxide content is re-used to prepare acceptable rods.

Difficulties were encountered in compacting one lot of 16 rods to acceptable density. Twelve of the 16 rods were rejected because of intrarod density variation. The oxide used to prepare these off-specification rods was ground for 13 hours, whereas, 4 hours grinding is usually sufficient to give the desired particle-size distribution in the fine (minus 200) fraction. Furthermore, there was an abnormal amount of moisture in the cubicle atmosphere during the period of time the oxide used to fill these off-specification tubes was being sized.

A material balance was made at the completion of a 100-kilogram throughput through the sol-gel and rod fabrication operations; a net loss of less than 3 per cent was experienced.

Mechanical failure of the ball mill and vibratory compaction units continues to be the major unsolved problem in the rod-fabrication facility. Efforts are being directed toward the solution to this problem.

Since the start of hot operations, it has been necessary to enter the rod fabrication cubicles a total of 25 times to make repairs to the equipment. Most of the cubicle entries were required to repair the ball mill, while other cubicle entries were made to repair the vibratory compaction equipment and the gamma scanner. Several maintenance and repair operations were necessary during the month. The ball-mill dumping mechanism was strengthened as much as possible by remote means. The alignment bolts holding the drive unit against the grinding jar loosened,

and a cell entry was required for its repair. The tungsten tip on the welder was changed remotely; however, entrance to the glove repair area to replace a broken bell jar was necessary. The detector tube on the gamma-ray densitometer failed and had to be replaced. The testing of the old tube by Instrument and Controls Division indicated that it was still operable, but with insufficient gain. While the testing was in progress, the tube seemed to be slowly recovering for a reason that is yet unexplained.

Approximately 60 of the Zircaloy-2 fuel tubes had been chemically etched prior to making the bottom end-cap weld. Such a large percentage of these rods have broken during compaction that the remaining ones were rejected and will not be used.

Pellet Fabrication.* The muffle furnace for fabricating the ThO_2-UO_2 pellets has been received and installed in the furnace glove box. The furnace is now undergoing tests to determine the need for auxiliary cooling for the glove box operation. The checkout of the remainder of the fabrication equipment will begin within the next month.

*Performed by Metals and Ceramics Division.

WASTE DISPOSAL DEVELOPMENT

Foam Separation Studies. -- The scavenging-precipitation foam-separation process for decontaminating low-radioactivity-level process waste water includes the following steps: precipitation of hardness by making the water 0.005 M each in NaOH and Na_2CO_3 and 2 to 10 ppm in Fe^{3+}; removal of the resulting solids in a gently stirred sludge column; and foam separation in a countercurrent column with sodium dodecylbenzene sulfonate as the surfactant. The surfactant-rich foam condensate, that also contains radiochemical impurities and solids, is recycled to the sludge column. By this arrangement there is only one waste stream, namely the sludge, which is drawn off continuously. In addition, surfactant consumption is minimized.

At the present time the performance of the sludge column is highly satisfactory. However, foam column operation has not yet been as good as was predicted from tests on the performance of a foam column under total recycle conditions.

During the first tests with this "plant" at a water flow rate in the sludge column of 20 gal ft^{-2} hr^{-1} and in the foam column of 60 gal ft^{-2} hr^{-1}, ORNL tap water spiked with Sr^{85} tracer was decontaminated by factors up to 8500. The dodecylbenzene sulfonate concentration in the decontaminated water had an average concentration of 5.6 ppm. Strontium decontamination across the sludge column achieved values up to 380 and across the foam column values up to 140. Decontamination across the sludge column was higher by a factor of about 25 than that previously observed for strontium decontamination from ORNL process waste water. Recycling of the foam condensate to the sludge column, thereby making water in the

sludge column about 17 ppm in dodecylbenzene sulfonate, did not seriously disrupt the mechanical operation of the sludge column. The only physical change caused by this recycle was the accumulation of a small quantity of solids on top of the otherwise clear water above the sludge upon prolonged operation (3 or 4 days).

Decontamination of water with respect to cesium was also tested in this apparatus. The test consisted of continuous addition of -230-mesh grundite clay (which strongly sorbs cesium) to Cs^{137}-spiked tap water at a rate of 0.4 to 0.6 lb per 1000 gal of water (in a tank, 5.5-min retention time) before the caustic-carbonate and Fe^{3+} water-softening chemicals were added. Cesium decontamination across the sludge column was 5.3 to 5.9. The foam separation column did not achieve any removal of soluble cesium; however, it increased the overall decontamination of cesium to 7.8 to 8.5 by removing entrained solids.

Foam Separation Engineering Studies. -- Experiment shows that foams are easily condensed while passing through an orifice with upstream-downstream pressure ratios of 2 or greater. The 0.015-,0.100-, and 0.250-cm-diam orifices all gave residual foam volumes of about 0.1% of the inlet volumes for foams with mean bubble diameters of 0.05 to 0.08 cm. The 24-in.-diam foam column (the proposed low-level-waste pilot plant column diameter) was operated at flows up to 80 liters per min of foam and 13 liters per min of liquid. The amount of channeling appeared acceptable at 5 liters/min or less liquid and 50 liters/min or higher gas flow rates; an improved liquid feed distributor will be necessary for higher liquid flow rates.

Engineering, Economic, and Safety Evaluation. -- Costs were estimated for permanent storage of calcined radioactive wastes in concrete vaults and in rooms mined out of granite formations. In comparison with previously estimated costs for storage in salt mines, costs for concrete vaults were five to seven times as much, and for storage in granite about twice as much. This economic advantage, as well as the greater safety it is believed to offer, makes salt the preferred choice.

Vaults for storage of calcined solid wastes would be similar in their gross features to many of the concrete secondary containments used for tanks built for storage of liquid radioactive wastes, in that they would be underground structures of reinforced concrete with about 10 ft of earth cover and a floor-to-ceiling height of about 15 ft. To make storage in vaults as safe as possible, they would be sealed completely from the surface, and space requirements were calculated by assuming dissipation of the heat of radioactive decay by conduction through the earth cover. Vaults of two types of concrete were considered: ordinary concrete, capable of withstanding 400 to 500°F, and "high-temperature concrete," capable of withstanding 1000°F.

Space requirements for the storage of calcined wastes in rooms mined out of granite formations are about the same as for storage in salt formations. However, mining costs are higher for granite because heavier equipment is required, drilling more difficult and slower, and costs of explosives are higher.

High-Level-Waste Disposal. -- A neutral ceramic developed for fixation of Purex waste containing sulfate appears to meet the requirements for stability, thermal conductivity, solubility, and low melting

point. Simulated Hanford FTW-65 waste solution was fixed in a microcrystalline solid by the addition of lithium, aluminum, calcium, and phosphate to the waste solution. Volume reduction from the unconcentrated waste was about 31. Sulfate loss was about 0.4%, due to entrainment. Thermal conductivity was in the range of 1.3 to 1.6 Btu hr^{-1} ft^{-1} $^{o}F^{-1}$ between 149 and 538°C. Leaching tests on specimens spiked with Cs^{137} gave rates which decreased to an apparently steady-state value of about 1.1×10^{-4} g cm^{-2} day^{-1} after about 30 days. The solid was mechanically strong and cracked into a few large pieces when broken, rather than shattering. The melting temperature was about 700°C. Corrosion of stainless steel in the melt at 950°C appeared to be no more severe than in air at the same temperature.

Non-sulfate Purex waste was incorporated into phosphate melts which were fluid at temperatures as low as 500°C and appeared to be true glasses. Corrosion of type 304L stainless steel at 950°C (more than 24 hr) in one such melt was significant but was not highly localized.

Corrosion tests on type 304L stainless steel, Hastelloy F, and titanium 45A all showed negligible ($\leqq$ 0.1 mil/month) corrosion rates for 840 hr of exposure in all phases of refluxing FTW-65 waste. There was no indication of local attack on either specimen of a titanium-304L stainless steel couple.

CHEMISTRY RESEARCH

Thorium Oxide Studies. -- Data from an ultracentrifugation study of a 1 M thoria sol of particles having a nitrogen BET specific surface area of 52 m^2/g indicate that a nitrate ion occupies 31 A^2 of thoria surface. For this thoria, therefore, the nitrate equivalence is 2.8×10^{-4} mole of nitrate ion per gram of thoria. For comparison it may be noted that Wadsworth et al. at the University of Utah found about 15 A^2 to be occupied by silicic acid on thoria. The "true" hydrogen ion concentration of solution in equilibrium with the above sol at the nitrate equivalence point was calculated to be 3.6×10^{-3} M. The calculated pH of the solution, when corrected for a minor activity coefficient deviation from unity, is 2.47. The pH of the sol read on a pH meter using a glass measuring electrode and calomel reference electrode was 3.9. The difference is attributed to the "suspension effect" and thoria adsorption on the glass electrode. As the ratio of moles of nitrate ion adsorbed to thoria surface area drops to about 78% of the foregoing equivalence value, the equilibrium hydrogen ion concentration drops to 5.0×10^{-4} mole/liter. The gel produced by centrifugation ceases to be dispersible to a true, stable colloid, and the acid concentration in the centrifugate rises to 6×10^{-4} mole/liter.

Low-temperature sintering properties of thoria gels are of basic importance to an understanding of how the sol-gel process produces dense ThO_2. The sintering properties of thoria gel may be related to the way water is held by the gel. Equilibrium and kinetic studies done by M. E. Wadsworth et al. at the University of Utah on gel dehydration indicate that water held by the gel in the temperature range from room

temperature to about 140°C is hydrogen bonded in a state very similar to that of liquid water. The principal difference seems to be that water in the gel is somewhat less ordered (slightly larger entropy) than it is in liquid water; further, the equilibrium temperature at one atmosphere water vapor partial pressure is 137°C instead of 100°C. In order for thoria to adsorb water by hydrogen bonding in a manner similar to that of liquid water, it is postulated that surface species such as hydroxyls, nitrates, and possibly carbonates are the adsorption sites at temperatures up to 140°C. The dehydration reaction is first order with respect to that fraction of water remaining at temperatures up to about 140°C.

Protactinium Chemistry. -- The high radiation level and unavailability of hot cell facilities for purifying the protactinium which was irradiated to prepare U^{232} have made it necessary to postpone its processing. Consequently it is possible to carry out further laboratory studies on protactinium separation chemistry. At present 1 to 2 g of the Pa^{231} are in a semipure state as the oxide. About 46 g are present in 10 liters of 8 M HCl-0.6 M HF.

The proposed purification involves complexing the fluoride present in the solution with Al^{3+} and loading both the Pa^{231} and the trace U^{232} as chloride complexes onto an anion exchange column. Experiments using 0.5 ml samples of the feed indicate that some dilution of the feed will be necessary to prevent precipitation of aluminum salts. The process tentatively proposed is to mix 1 volume of feed (8 M HCl--0.6 M HF) with 1.5 volumes of 6 M HCl--1 M $AlCl_3$ immediately before loading onto the anion column.

A series of extractions with di(2-ethylhexyl)phosphoric acid was carried out to determine whether any significant separations could be achieved by this procedure. The results indicated that there was no separation of protactinium from uranium, thorium, or niobium. The possibility of separations in a scrub or stripping step has not been investigated.

Some progress has been made in the adjustment of the feed solutions to allow the sorption of thorium on a cation exchange column without any sorption of protactinium. In one series of experiments, diluting the feed to 2 M HCl and adding one mole of boric acid per mole of hydrofluoric acid resulted in sorption of 63% of the thorium onto a Dowex-50 column without any loading of the protactinium. Work is continuing on this problem.

Since protactinium and niobium can be separated by chromatographic elution from a Dowex-1 column, a feed containing approximately 3 mg of protactinium and 7×10^6 gamma counts per min of $Zr\text{-}Nb^{95}$ was loaded onto a 3-mil column and eluted with 8 M HCl--0.2 M HF. The resulting product contained more than 90% of the protactinium and no detectable $Zr\text{-}Nb^{95}$.

Attempts to precipitate protactinium from the feed by dilution with water were unsuccessful. Samples, both with and without $AlCl_3$, were diluted to 2 M HCl. These were then centrifuged and the supernatant analyzed. No significant change in alpha or gamma activity was noted.

Equipment Decontamination. -- Fission-product deposition samples that had been exposed in an ORR poolside experiment to helium contaminated with fission products from neutron-irradiated uranium carbide-thorium carbide fuel spheres were found to have surface deposits relatively

low in barium and iodine. Also, little iodine has been found so far in loop deposits, although amounts of barium were relatively high. Explanations have not yet been found. In laboratory tests, however, Ba^{140} (added as chloride solution) has so far been virtually nonvolatile from graphite in helium or hydrogen at 1100°C, and iodine has not been appreciably deposited on steel above about 400°C.

An inexpensive new method for the low-corrosive decontamination of carbon steel at room temperature is under study. The method employs a preliminary 5-min treatment of the steel with 0.02 M oxalic acid to dissolve rust and condition the surface, followed by gradual addition of hydrogen peroxide up to about 0.05 M during the next 3 to 5 min. Total corrosion is about 0.05 mil, with decontamination factors on 400°C-baked $Ba\text{-}La^{140}$ of 400 to 800.

TRANSURANIUM ELEMENT PRODUCTION

Chemical Process Development: Separation of Curium from Americium at High-Activity Levels. -- Separation of curium from americium by chromatographic elution from a spring-loaded cation exchange column with ammonium α-hydroxyisobutyrate at activity levels of 50 w/liter was achieved. Two milligrams of Cm^{242} and 4 mg Am^{241} were loaded on a 20-ml column of Dowex 1-X8 (-400 mesh) resin at 80°C. The curium and americium were eluted with 0.4 M ammonium α-hydroxyisobutyrate at pH 4.2 at a flow rate of 0.3 ml cm^{-2} min^{-1}. Gassing problems were controlled, and separation of the bed was prevented by springloading the resin column. A 90% Cm recovery contaminated with 10% of the Am was accomplished.

Separation of curium from americium was also accomplished by chromatographic elution from a spring-loaded anion exchange column with lithium nitrate at activity levels of 100 w/liter. The characteristic cherry-red glow from the activity was observed to separate into two bands--a white and a red. The white glow was associated with the curium, while the red was due to americium excitation. The separation factor was 1.87, and results indicate that a complete curium-americium separation could be achieved with about 1% cross contamination.

Dissolution of Prototype HFIR Targets. Four unirradiated prototype HFIR targets were processed for plutonium recovery. These targets consisted of a mixture of high-fired PuO_2 and aluminum powders which have been compacted. The aluminum was readily dissolved in 1.2 M NaOH--1.5 M $NaNO_3$. Plutonium losses during aluminum dissolution averaged 0.7 mg/liter (0.002%). The PuO_2 was dissolved in 14 M HNO_3--0.2 M HF under reflux. Plutonium product, concentrated to 24 g/liter plutonium,

contained 0.02 g of aluminum per liter of solution. This method may be useful for reclaiming Pu^{242} from HFIR targets that do not meet specifications for irradiation.

Corrosion Studies. -- The susceptibility of Zircaloy-2 to hydrogen pickup in certain boiling acid solutions was further substantiated. In previous tests, 125-mil-thick specimens of the alloy contained 89 ppm of hydrogen after 1000 hr in boiling and oxygenated 6 M HCl and 440 ppm after a similar period in boiling and oxygenated 6 M HCl--0.1 M HNO_3 solution. The heat initially contained between 38 and 53 ppm of hydrogen. In the present tests, a different heat of the alloy, in the form of 10-mil-thick strip, was used; the initial hydrogen content was 260 ppm. After a 1000-hr exposure, the bulk hydrogen content of a specimen in boiling and oxygenated 6 M HCl was 5300 ppm, whereas 2600 ppm were found in a specimen exposed for 1000 hr in boiling and oxygenated 6 M HCl--0.1 M HNO_3. Both specimens underwent brittle fracture during bending after test.

Zircaloy-4 containing less than 20 ppm of nickel corroded ten times faster than a 125-mil-thick heat of Zircaloy-2 in boiling and oxygenated 6 M HCl solution. After 1000 hr, the Zircaloy-4 rate was 22.8 mils/yr compared with 2.4 mils/yr for Zircaloy-2. The bulk hydrogen content of the Zircaloy-4 specimen after test was 130 ppm, compared with an initial value of 19 ppm. The hydrogen content of the companion Zircaloy-2 specimen was 89 ppm after test, whereas the initial content varied from 38 to 53 ppm.

ISOTOPE DEVELOPMENT PROGRAM

Recovery of Fission Products. -- By the use of silver-catalyzed ammonium persulfate as oxidant, cerium was oxidized and extracted effectively with di(2-ethylhexyl)phosphoric acid (D2EHPA) to give separation from other fission-product rare earths. The feed solution was the rare-earth strip product (1.2 M in free nitric acid) from the D2EHPA process for recovering strontium and mixed rare earths from Purex 1WW waste. The oxidation of cerium was much more effective in the presence of the solvent phase than when the cerium was oxidized prior to extraction. The cerium extraction coefficient (1/1 phase ratio) in 1 hr of contact time at 50 to 55°C was about 25.

Of several stripping agents examined for recovering technetium from Aliquat 336, a quarternary amine extractant, only perchloric acid (2 to 6 M) gave stripping coefficients greater than 1.

Curium-242 Preparation: Recovery: Control of Acidity in High-Activity-Level Tramex Feed. -- The sensitivity of separations by the Tramex process to small changes in acidity makes control of acid losses through radiolysis exceptionally important. Studies of this problem are continuing.

Preliminary investigations were made to determine whether hydrazine·monohydrochloride or formaldehyde added to high-activity-level Tramex feed would stabilize the acid at a concentration in the 0.01 to 0.1 N range, which is necessary for satisfactory extraction. When $N_2H_4 \cdot HCl$ was present in high-activity-level Tramex feed, the G value for H^+ production was about 1.4. In the absence of $N_2H_4 \cdot HCl$, the G value for H^+ destruction is about 1.4. This G value for H^+ production is equivalent

to an acid increase of about 0.1 mole per liter per day for a Cm^{242} concentration of 10 w/liter. Presumably the hydrazine reacts to convert chlorine in radiolysis products to HCl and at the same time releases HCl chemically bound in the $N_2H_4 \cdot HCl$ salt.

When 1% formaldehyde was present in 10 M LiCl containing 10 w of Cm^{242} per liter, the H^+ increased only 0.066 mole per liter in seven days. This is equivalent to an acid-production G value of about 0.14. These results indicate that acid concentration in Tramex feed can be satisfactorily controlled by the addition of small amounts of formaldehyde. Additional study is needed to confirm the validity of these conclusions.

Full-Activity-Level Tramex Flowsheet Test. A total of five hot runs have been made at Cm^{242} power levels of 5 to 10 w/liter. Operating difficulties were slight except for the last run, in which the air lift pump for hot feed became inoperable. Although none of the runs was made at proper conditions for both high curium recovery and complete fission product decontamination, the results indicate that the Tramex process should be capable of producing a high yield of acceptable product.

No effect of radioactivity was noted on the solvent extraction operation at 10 w/liter; however, radiolysis of the low-acid feed did cause precipitation somewhere between 28 and 40 hr after feed adjustment.

Effect of Nitrate on Extraction in the Tramex Process. The addition of small amounts of Alamine $336 \cdot HNO_3$ to Alamine 336·HCl-diethylbenzene is being investigated as a possible means of increasing actinide distribution coefficients. With higher distribution coefficients, control of Tramex feed acid concentration should be less critical.

Distribution coefficients between 0.6 M Alamine 336·HCl-diethylbenzene and 10 M LiCl--0.15 M $AlCl_3$ were 6 for americium and 0.05 for europium. When the extractant was 0.5 M Alamine 336·HCl-0.1 M Alamine 336·HNO_3-diethylbenzene, distribution coefficients were increased to 22 for americium and 1.2 for europium. The effect of free acid in this system is being investigated.

Laboratory Demonstration of Chloride-to-Nitrate Conversion for Curium-242 Product. Curium-242 product from the Tramex process will be contained in approximately 12 liters of 8 M HCl. The proposed method of converting this to a nitrate solution is to evaporate to 4 liters, add 4 liters of concentrated nitric acid, and evaporate to 4 liters. This process is to be repeated two more times.

This conversion method was tested at 1/10 scale in tantalum equipment with simulated feed containing mixed rare earths as substitutes for americium and curium.

Chloride concentration of the product was reduced to 1 or 2 ppm after the second nitric acid boil-off and to less than 1 ppm after a third boil-off. The final product was approximately 14 M HNO_3 containing 0.5 g of rare earths per liter. Noncondensable acid reaction products (probably nitrosyl chloride) were readily scrubbed from the off-gas with dilute caustic. From all three boildowns a total of about 5.5 equivalents of acid were collected in the caustic trap for each liter of product.

Ruthenium added as Ru^{3+} chloride did not volatilize during the conversion to nitrate. Methods to promote ruthenium volatilization are being investigated.

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