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ORNL
CENTRAL FILES NUMBER

59-6-13

DATE: June 1, 1959

COPY NO. 9

SUBJECT: Power Reactor Fuel Reprocessing Status Report of
ORNL Chemical Technology Division for May 1959

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ABSTRACT

Process development studies are reported on Sulfex, Zirflex, Darex, Fused Salt-Fluoride Volatility, mechanical processing, long range studies and the pilot plant.

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POWER REACTOR FUEL REPROCESSING STATUS REPORT OF
THE ORNL CHEMICAL TECHNOLOGY DIVISION FOR MAY 1959

Sulfex Process. In a 4-hr decladding test in boiling 6 M H_2SO_4 of a Yankee fuel pin (stainless steel-clad UO_2 pellets) irradiated to 800 Mw and decayed four months, U and Pu losses were 0.03% and 0.07%, respectively, confirming previous loss data. Spectrographic analysis of the washed solid residue from the decladding and pellet dissolution showed only a trace of uranium. In all cases where the stainless steel was passivated to 6 M H_2SO_4 , wrapping the pin with iron wire initiated the reaction. Zinc and chromous sulfate are being investigated as chemical depassivators.

The stainless steel tube that contains the thorium oxide-uranium oxide pellets of the Consolidated Edison fuel may be dissolved in 6 M H_2SO_4 . The uranium loss from pellets of 95.5% ThO_2 - U_3O_8 refluxed in 6 M H_2SO_4 in the absence of stainless steel for 6 hr (1 g of pellets per 5 ml of acid) was 0.5%. In identical tests with 95.5% ThO_2 - UO_2 the uranium loss was only 0.02%. The presence of 0.5 M HNO_3 in the 6 M H_2SO_4 did not increase the uranium loss from ThO_2 - U_3O_8 pellets. Losses from ThO_2 - U_3O_8 pellets were <0.1% when stainless steel was simultaneously dissolved at a rate $>10 \text{ mg/cm}^2 \cdot \text{min}$.

Tests on corrosion during decladding in 6 M H_2SO_4 and core dissolution in 13 M HNO_3 -0.04 M HF (Thorex dissolvent) were continued. After 1000 hr exposure to boiling 13 M HNO_3 -0.04 M HF, welded Nionel, heat-treated at 1950°C and air-quenched, showed rates of 1.8 and 4 mils/mo from weight loss and metallographic examination data, respectively. In 8 cyclic Sulfex-Thorex dissolutions, Nionel corrosion rates varied between 1.8 and 2.7 mils/mo. In boiling 6 M H_2SO_4 titanium was corroded at very high rates.

Zirflex Process. In Zirflex process corrosion tests, Nionel and Type 309Nb stainless steel were corroded in boiling 6 M NH_4F -1.0 M NH_4NO_3 -0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ -0.05 M Na_2SiO_3 at maximum rates of 6.1 and 4.1 mils/mo, respectively, in 500 hr exposure. Monel was corroded at rates of 17-23 mils/mo during four successive 24-hr exposures to boiling 1 M HF-0.06 M H_2O_2 .

Darex Process for APPR Fuel. At room temperature air sparging of a solution of APPR fuel in 5 M HNO_3 -2 M HCl for 12 hr decreased the chloride only from 0.65 to 0.41 M. At boiling temperature in 8 M HNO_3 air sparging decreased the chloride ion concentration to the same extent as nitrogen sparging. Filtration of the chloride-free solution of APPR fuel through bare porous metal appears feasible in a production plant, no difficulty in recovering uranium from the filter cake being anticipated. In a typical experiment with 10 liters of solvent extraction feed

from APPR type Darex head end treatment, 35.6 cu in. of wet filter cake was collected on a 0.66 sq ft filter. The cake was washed three times with 5 liters of water per wash. The uranium loss after one wash was <0.1% and after three washes was 0.005%.

Several gelation and filter aid media were tested for removing silica from dissolver product, prior to chloride removal, at reasonable filtration rates. The best were 0.004 M HF with Celite 545 and 0.004 M HF alone; Celite 545 alone, activated alumina, ammonium molybdate, and silica gel were all unsatisfactory. Freezing of the solution was also ineffectual. Centrifugation in a 5-in.-dia solid-bowl centrifuge at 3000 rpm completely removed siliceous material at centrifuge flow rates up to 400 cc/min.

A 2.5% TBP flowsheet study indicated that 5.5 extraction and 3.5 stripping stages are required for satisfactory uranium recovery.

Darex Process for Consolidated Edison Fuel. Consolidated Edison fuel samples (stainless steel-clad $\text{ThO}_2\text{-UO}_2$) were declad with 4 M HNO_3 -2 M HCl with 0.2 and 0.02% loss of uranium and thorium, respectively. With 5 M HNO_3 -2 M HCl , uranium losses were 0.3-0.4%. Losses were not increased by exposure of the core oxide to depleted Darex solution (1.3 M HNO_3 -1.5 M HCl -50 g of stainless steel per liter) for times up to 3 hr at boiling.

In scouting tests Consolidated Edison fuel dissolved completely in dilute aqua regia containing fluoride catalyst, producing a solution from which uranium and thorium may be recovered by solvent extraction. In preliminary Thorex solvent extraction experiments aluminum ion in excess of that required to complex the fluoride ion to decrease corrosion in the dissolver was not required for salting. This differs from the processing conditions for Th metal where $\text{Al}(\text{NO}_3)_3$ must be added. With the stainless steel-containing fuel salting strength is provided by the dissolved stainless steel.

Aqua regia decladding and core dissolution in boiling Thorex dissolvent (13 M HNO_3 -0.04 M HF) is being considered. Titanium, a possible material of construction, was corroded in the vapor phase at a rate of 8.1 mils/mo in 756 hr exposure. When 0.04 M Al^{3+} was present, the maximum rate was 1.7 mils/mo. With <0.04 M Al^{3+} , pitting occurred. After 13 consecutive Darex decladding-Thorex dissolvent dissolutions, the maximum corrosion rates of titanium coupons were <0.2 mil/mo. In a 253-hr test, titanium A-55 in the vapor and liquid phases of a modified boiling Thorex dissolvent (13 M HNO_3 , 0.04 M F^- , 0.1 M H_2BO_3) containing 0.0, 0.5, and 1.0 M thorium from dissolved Consolidated Edison pellets was corroded at a maximum rate of 0.6 mil/mo. The boric acid might be a useful inhibitor for vapor-phase corrosion.

Thorium and uranium were >99.9% extracted with 42.5% TBP in Decalin from a solution containing 1.5 M Th, 0.085 M U, 4.0 M H, 0.1 M Al, and 0.04 M F. Extraction with 42.5% TBP in Amsco was unsatisfactory because of third phase formation. The scrub in both cases was 5 M HNO_3 . Uranium only was extracted under similar conditions with 5% TBP in Amsco.

Darex Process for Yankee Fuel. In a bench-scale test with unirradiated Yankee fuel samples (stainless steel-clad UO_2) the complete Darex standard flowsheet was successfully demonstrated; chloride was removed to 440 ppm before dilution to flowsheet concentrations. With a fuel pin irradiated to 1000 Mwd/t and decayed 4 months, the waste and recycle-acid streams contained approximately 0.01% of the activity in the dissolver solution. A small quantity of solid residue from the dissolution and feed-adjustment steps, principally iron and silica as shown by analysis, contained no uranium. Over-all heat-transfer coefficients were 200-300 Btu/hr.ft². F in a prototype steam-heated titanium feed-adjustment tank during the mixed-acid-removal and recycle-acid-recovery steps.

Fused Salt--Fluoride Volatility Process. Fuel elements with high zirconium contents may be reprocessed by dissolution in molten fluoride in the presence of HF prior to volatilizing uranium with fluorine. In three dissolution experiments at 700°C in an INOR-8 dissolver using the 43-57 mole % NaF-LiF salt system, the effect was determined of HF feed rate and initial ZrF_4 content on the dissolution rate of Zircaloy-3. In runs at 2.5 and 6 lb of HF per hr, average dissolution rates were 1.9 and 2.7 mg/(cm² of original surface) (min) with no initial ZrF_4 . When the experiment with a feed rate of 6 lb/hr was repeated with 13 mole % ZrF_4 initially present, the average dissolution rate decreased to 2.0 mg/(cm²) (min). The melting point of the salt containing 13 mole % ZrF_4 is approximately the same as zirconium-free salt (650-660°C), but the dissolution temperature could be decreased to 650°C in the range 16-56 mole % ZrF_4 with a corresponding decrease in corrosion rates.

At higher temperatures zirconium or Zircaloy reacts with HF in the absence of fused salt. A 9-plate Zircaloy-3 fuel assembly was reacted with HF at 1025°C at an average reaction rate of 6 mg/(cm²) (min) based on the initial area (0.72 ft²). The average HF utilization was 47%. The run was terminated after 85% reaction (3 hr) in order to measure the remaining reacting area (0.16 ft²).

Mechanical Processing. Dummy Yankee fuel elements, UO_2 pellets clad in 0.4-in.-o.d. 0.1-in.-thick-wall stainless steel tubing, were sheared to 0.5-, 1-, 2-, 3-, 4-, and 5-in. lengths and were subsequently leached free of uranium with 173% excess of boiling 10 M HNO_3 . The leaching times, 40-240 min, were greater by a factor of 2 than with 150% excess of 10 M HNO_3 .

Long Range Studies. Previous studies have shown that nitric oxide may be used to induce the volatilization of chloride from nitrate solutions at room temperatures. Nitric acid was also found to be transferred by a similar reaction.

Pilot Plant. An additional 8 metric tons of BNL irradiated uranium fuel, containing 3.6 kg of plutonium, was processed. Based on losses from the plant, uranium and plutonium recoveries were 99 and 99.25%, respectively. The plutonium product met gross gamma specifications. The uranium product gross gamma contamination was higher than specifications by a factor of 3 but was acceptable for shipment to Y-12. Uranium product decontamination was improving as the run progressed.

Miscellaneous. In corrosion tests to determine the possibility of using Darex equipment for U-Al dissolution, four 72-hr exposures of titanium to boiling 8 M HNO_3 - $0.05\text{ M Hg(NO}_3)_2$ resulted in an average corrosion rate of 0.73 mil/mo. In tests to determine the possibility of using 304L stainless steel piping for transferring cold (125 F) Darex dissolver solutions, this alloy was occasionally activated, resulting in serious corrosion. Probably the piping will have to be titanium.

From a simulated Darex-Foreign Research Reactor (U-Al alloy) fuel dissolution product ($2\text{ M Al(NO}_3)_3$ - 2 M HCl) chloride was removed to 10 ppm by the standard Darex procedure.

In a 0.15 M acid-deficient Redox solvent extraction run, U was extracted from a typical low enrichment Darex fuel solution (0.4 M U, 0.8 M stainless steel, 0.004 M Si) with hexone in a 2-in.-dia x 25 ft high (21 ft extraction, 4 ft scrub) column packed with 1/4- by 3/8-in. stainless steel Raschig rings with 0.04% loss. This is 20 times greater than the loss in the same columns with Redox feed prepared from fuel containing no stainless steel. The feed/scrub/solvent flow ratio was 1/0.24/2.5. Flooding occurred at a flow rate of 485 gal/hr.ft². The extraction HETS was approximately 2 ft.

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