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ORNL Chemical Technology Division for April 1959

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ABSTRACT

Process development studies are reported on Sulfex, Zirflex, Zircex, Darex, alternative aqueous processes, mechanical processing, solvents, pilot plant and waste treatment.

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

Sulfex Process. Two prototype Yankee (stainless steel--clad UO_2) pins irradiated to 500 and 775 Mwd/t, respectively, were declad with 200% excess boiling 6 M H_2SO_4 . Maximum uranium and plutonium losses, determined in the presence of undissolved stainless steel end caps, to the decladding solution were 0.012 and 0.05%, respectively. Passivation of the stainless steel cladding was more difficult to overcome than on autoclaved unirradiated specimens, but when wrapped with iron wire they dissolved in 4 hr in fresh 6 M H_2SO_4 . This procedure is unacceptable in a process. Other work has indicated that dissolution of stainless steel would not start if the H_2SO_4 contained more than a few grams per liter of dissolved stainless steel or more than 0.01 M nitrate. Dissolution of the declad UO_2 in boiling 10 M HNO_3 was incomplete in 4 hr.

In Consolidated Edison fuel tests, type 304L stainless steel cladding was passivated in boiling 6 M H_2SO_4 containing >0.015 M HNO_3 . In 3 M H_2SO_4 --0.1 M HNO_3 , passivation did not occur, but the dissolution rate was lower. The passivation was easily broken in 3 and 6 M H_2SO_4 containing 0.2 M HNO_3 by steel wool in contact with the specimen. In 15 decladding tests on unirradiated prototype Consolidated Edison fuel with 6 M H_2SO_4 , the soluble uranium loss varied from 0.02 to 0.24%, averaging 0.08%, and with 80% of the samples 0.10% or less. The losses reported are probably not representative of losses from specification grade fuel, since the uranium oxide in the prototype fuel analyzed approximately $\text{UO}_{2.10}$ and the tube had been seal-welded in air rather than helium.

Continuing corrosion tests on the Sulfex-Thorex system indicate that long boiling of 13 M HNO_3 --0.04 M HF in Nionel results in oxidation of chromium to Cr(VI) and in intergranular attack on the Nionel. Over-all rates after 1000 hr were as high as 6.2 mils/month, vs. 2.1 mils/month when all chromium was in the Cr(III) state. In 3.5 M H_2SO_4 containing 50 g/liter of dissolved stainless steel Nionel was corroded at a maximum rate of 1.1 mils/month.

Zirflex Process. In corrosion tests the addition of 0.05 M borate and 0.05 M silicate lowered the corrosion rates of Nionel and type 309 stainless steel in boiling 6 M NH_4F --1.0 M NH_4NO_3 from 12 to 6 and from 7.2 to 4.0 mils/month, respectively.

Zircex Process. In the original Zircex process complete dissolution of the uranium from the HCl hydrochlorination residue in HNO_3 was never achieved. Losses ranged from 1% with the EBWR (low enriched U-235) fuel to 6% with the STR (highly enriched U-235) fuels. In recent tests in which both the HNO_3 -leached and unleached residues were chlorinated at 550-600°C with CCl_4 , the uranium loss was <0.01% for both fuels. Secondary advantages of the use of CCl_4 as a final chlorination agent are reduced corrosion and elimination of possible explosions between U-Zr alloys and HNO_3 .

Darex Process. Results of tests on removal of chloride from APPR-Darex dissolver product made under flowsheet conditions indicated that air sparging assists in chloride removal, removal by sparging is complete in <6 hr, and the HNO_3 concentration required to remove chloride to 50 ppm, with or without sparging, is > 9 M. Prior to chloride removal silica was apparently in a completely soluble form, and the solution was filtered through a 4-in. sand bed at a 6-in. solution head at an average rate of 51 ml/cm².min. During chloride removal, highly hydrated silica precipitated, and after volume adjustment, the average filtration rate of the chloride-free solution was 0.09 ml/cm².min. Porous metal filter elements, 20 μ, in which filter aid had not been used, were satisfactorily regenerated with boiling 25% NaOH solution even after 4 days' drying prior to cleaning.

An over-all heat transfer coefficient of 450-500 Btu/hr.ft².°F was measured in a titanium feed adjustment tank of the proposed APPR pilot plant design at a boiling water to steam temperature difference of 40-55°F.

In corrosion tests titanium tubes exposed to boiling 2 M HCl--5 M HNO_3 at 135°C for 2000 hr corroded at maximum rates of 1.5-2 mils/month. Stressed and welded specimens of types 304 ELC and 347 stainless steel in boiling 3 M HNO_3 containing 60 g/liter of dissolved stainless steel showed severe intergranular attack, though maximum over-all rates were on the order of 5 mils/month. This attack appears to be independent of chloride concentration, at least up to 800 ppm.

In tests on decladding of prototype Consolidated Edison (stainless steel--clad UO_2 - ThO_2) fuel pins with 5 M HNO_3 --2 M HCl, uranium losses were 0.3-0.4% in a 2-hr decladding run.

In preliminary tests on titanium as a material of construction for a Darex-Thorex head-end process, welded titanium in boiling 13 M HNO_3 --0.04 M HF was corroded at a maximum rate of 11.8 mils/month for a 24-hr exposure. In the presence of varying amounts of Al(III) and Th(IV), maximum rates as low as 0.5 mils/month were observed for 240-hr exposures.

Alternative Aqueous Processes. Processing problems arising from the presence of lead as the bonding agent in Borax-IV fuel were studied. In dissolving the Borax-IV Al-Ni alloy cladding in mercury-catalyzed nitric acid, rates were very low when lead was present unless the mercuric ion concentration was about 0.5 M. If not removed during decladding, lead seriously limited the uranium and thorium concentrations that could be attained by dissolution of the core in 13 M HNO_3 --0.04 M NaF --0.04 M $\text{Al}(\text{NO}_3)_3$ because of the very low solubility of lead nitrate in concentrated nitric acid.³

Mechanical Processing. The replacement cost for saw blades for removing the inert end adapters of fuel assemblies, based on experimental wear ratios, was calculated as varying from \$0.12 per element for the ORNL Gas Cooled Reactor fuel to a maximum of \$1.20 for the Consolidated Edison Reactor fuel.

In core leaching studies, unirradiated 0.4-in.-dia stainless steel--clad UO_2 prototype fuel elements were sheared into 0.5-, 1-, 2-, and 2.75-in. lengths and completely batch leached with 10 M HNO_3 in 30, 45, 60, and 75 min, respectively. In all tests an acid volume to initial UO_2 weight ratio of 2.5 ml/g (150% excess) was used.

Solvent Studies. In countercurrent batch extractions of synthetic Consolidated Edison fuel solution first cycle decontamination factors were 3.5×10^5 from gross γ , 2.9×10^4 from Ru γ , 1.8×10^5 from Zr-Nb γ , and 1.2×10^6 from TRE β ; second cycle factors were 7.6×10^4 from gross γ , 3×10^4 from Ru γ , 6.3×10^4 from Zr-Nb γ , and 1.4×10^5 from TRE β . Passage of the feed through silica gel at 50°C gave a Zr-Nb decontamination factor of 37. The use of cadmium as a neutron poison will not be limited because of its extraction by 5% TBP; the maximum Cd DC o/a found under a wide variety of conditions was less than 0.001.

In engineering-scale tests in 2-in.-dia glass-packed columns, the flooding rate for a Darex-Redox type solvent extraction flowsheet was 330 gal/hr.ft² when the feed contained 0.015 M Na_2SiO_3 . Addition of 100 ppm of Mistron (an insoluble calcium-magnesium silicate powder) increased the column capacity by a factor of 2.5.

Radiolysis studies were made under subcontract by Stanford Research Institute on solvents consisting of 30 g of TBP diluted to 100 cc with each of the following solutions: (1) 5 and 10 volume % isopropyl biphenyl in Amsco 125-82; (2) 5 and 10 volume % naphthalene in Amsco. Each solution was contacted with 2 M HNO_3 before irradiation. Neither aromatic compound appreciably affected the total gas or monobutyl phosphoric acid (MBPA) produced by 200 or 400 watt-hr/liter irradiation. The MBPA G values of 0.42 to 0.80 (molecules of MBPA per 100 ev of energy absorbed) support previous conclusions that nitric acid increases the rate of hydrolysis of the predominant radiolysis acid, dibutyl phosphoric acid, to MBPA.

Pilot Plant. The plant was on-stream 15 days during this month and a total of 4 metric tons of irradiated uranium from BNL and Savannah River reactors was processed. The down-time of 15 days was for equipment replacement and plant clean-out between programs.

Gross gamma decontamination factors in solvent extraction were generally lower than expected and flowsheet changes will be made to improve decontamination. In the co-decontamination cycle gross gamma decontamination factors decreased from 2200 to 500 during 12 days of operation while processing Savannah River fuel. The major fission product contaminants in the product from each cycle were Zr-Nb. Based on measured losses from the plant, product recoveries for uranium and plutonium were 96 and 98%, respectively. Unusually high losses during this month were caused by plant clean-out and planned high losses to satisfy the requirements of a special program.

Waste Treatment. Conversion of high-level liquid wastes by evaporation and calcination to a more readily disposable solid form is under study. Phase compositions were determined as a function of temperature for the evaporation of TBP-25 ($\text{Al}(\text{NO}_3)_3\text{-HNO}_3$) wastes to 146°C. Little nitrate decomposition occurred below 146°C but the final solution was very viscous. The condensate volume and weights were about 80 and 70%, respectively, of those of the original waste. The condensate contained about 55% of the total nitrate and 100% of the original free nitric acid. The density of the final solid product after calcination at 650°C was 0.5 g/cc as compared to a density of 1.0-2.0 obtained with ferric oxide solids in earlier experiments.

The thermal conductivity and thermal diffusivity were determined as a function of temperature at the center of an 8-in.-dia cake of Darex waste calcined at about 900°C. The thermal conductivity increased from 0.042 to 0.11 Btu/hr.ft. F when the average temperature increased from 120 to 480°F. For the same temperature range the thermal diffusivity increased from 0.0037 to 0.0061 ft²/hr. These results show that values assumed in previous theoretical predictions of temperature maxima in stored calcined waste were conservative.

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