OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE NUCLEAR COMPANY
Division of Union Carbide Corporation

Post Office Box X
Oak Ridge, Tennessee

MASTER

~~DISTRIBUTION LIMITED TO~~
~~RECIPIENTS INDICATED~~
EXTERNAL TRANSMITTAL
AUTHORIZED

ORNL
CENTRAL FILES NUMBER

59-6-128

DATE: June 30, 1959
SUBJECT: Power Reactor Fuel Reprocessing Status Report of
ORNL Chemical Technology Division for June 1959
TO: F. L. Culler
FROM: H. E. Goeller and W. H. Lewis

COPY NO. 11

ABSTRACT

Process development studies are reported on Sulfex, Darex, Perflex, MSR fuel, Borax IV fuel, graphite-containing fuel, mechanical processing and the pilot plant.

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

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

Sulfex Process. In tests on depassivation of the clad of prototype Yankee Atomic fuel specimens (stainless steel clad UO_2), iron wire in contact with the passive clad surface consistently initiated complete dissolution of the clad in boiling 6 M H_2SO_4 . The passive film was also destroyed by 15-min exposure of the pins to concentrated chromous sulfate at 85°C. Soluble uranium and plutonium losses during the 30-min required for decladding of irradiated Yankee fuel specimens with boiling spent 6 M H_2SO_4 were a maximum of 0.05% for fuel irradiated to 1440 Mwd/t uranium. However, uranium and plutonium losses were as high as 20% when irradiated core material was exposed to boiling fresh decladding solution, in the presence of oxygen, for 24 hr.

The rate of dissolution of sintered 95.5% ThO_2 - UO_2 pellets (Consolidated Edison fuel) in 200% excess of boiling 13 M HNO_3 -0.043 M NaF -0.1 M $\text{Al}(\text{NO}_3)_3$ decreased from 50% in 1 hr with no sulfate present to 1% in 1 hr when the sulfate concentration was 0.3 M.

Radiation-induced uranium losses from UO_2 - ThO_2 in 6 M H_2SO_4 were less than 0.3% in 3 hr. The percentage increase in losses was inversely dependent on temperature, with 70% increase in loss at 35°C but only 40% increase at 75°C. In a single run in boiling 6 M H_2SO_4 with a crushed reactor-irradiated pellet, uranium losses were about 3% after 3 hr. Much acid-insoluble thorium sulfate was formed during this run.

The presence of boric acid, a possible neutron poison, did not affect the dissolution time of ThO_2 - UO_2 pellets in Thorex dissolvent (13 M HNO_3 , 0.1 M Al , 0.04 M F). The solubility of boric acid in Thorex dissolvent increased from 0.26 M at 23°C to 1.18 M at 85°C. Thorex dissolvent was steam stripped to acid deficiency at 120°C. Without steam stripping the solutions must be heated above 150°C to remove the free acid. The corrosion rate of Nionel was 2.3 mils/mo after 15 Sulfex-Thorex cyclic dissolutions.

Darex Process. The Darex reference flowsheet was used successfully on APPR and Yankee Atomic prototype fuel solutions to remove chloride to 70 ppm. The presence of titanium had no adverse effect. An average overall heat transfer coefficient of 250 Btu/hr.ft². F was determined for the system condensing steam - 0.090-in. Ti - Darex solution in a 1/25 scale pilot plant scale (8 kg U^{235} per day) Darex still.

Approximately 40% of the silica remaining after Darex dissolution of APPR fuel had a particle size of >13 μ , which was removed by medium-size fritted glass but not by 30-mesh sand. The remainder of the silica passed through fine fritted

glass. Addition of 0.4 g of gelatin per liter of dissolver solution at 60°C permitted removal of 50% of the silica by medium-fritted glass immediately and an additional 10% after 24 hr. Addition of 0.005 M HF during dissolution resulted in immediate removal of 60% of the silica and 100% after 2 days by medium fritted glass filtration.

Perflex Process. In the Perflex process uranium-zirconium alloy fuels are dissolved in aqueous $\text{HF-H}_2\text{O}_2$. In corrosion studies with Monel and Inor-8 neither was sufficiently corrosion-resistant for use as a process vessel. In 1 M HF-0.06 M H_2O_2 Monel corroded at a maximum rate of 157 mils/mo in 4 hr; the rate was decreased to 57 mils/mo by contact with dissolving zirconium and blanketing with nitrogen. In 1 M HF-0.06 M H_2O_2 Inor-8 corroded at a maximum rate of 47 mils/mo in 24 hr.

MSR Fuel Processing. Modification of the MSR fuel process to obtain decontamination of recycle Li^7F from cesium, and to recover uranium by a low temperature volatility method appears possible. The present method consists of fluorination of UF_6 from the molten LiF-BeF_2 base salt at high temperature with F_2 , followed by dissolution of the salt in 90-100% HF. This results in good decontamination of the Li^7F from rare earths and neptunium. A test showed that appreciable decontamination from cesium was obtained by lowering the HF concentration to about 40% by either evaporation or addition of water. In one test when the HF concentration was lowered from 90% to 42% by evaporation, 97% of the LiF precipitated, leaving over 65% of the cesium in solution. HF-ClF_3 mixtures were used to achieve fluorination of UF_4 while at the same time achieving dissolution of Li^7F . The UF_6 formed in this manner at a low temperature and with little corrosion could be flashed off and recovered from the HF recycle by distillation or absorption.

Borax IV Fuel. The presently preferred method for processing Borax-IV fuel is removal of the aluminum clad with boiling 2 M NaOH - 1.78 M NaNO_3 , dissolution of the lead bond in 12- M HNO_3 , and dissolution of the sintered $\text{ThO}_2\text{-U}_3\text{O}_8$ core in boiling 13 M HNO_3 -0.04 M NaF-0.1 M $\text{Al}(\text{NO}_3)_3$. The initial rate of dissolution of lead foil increased from 3.3 to 15.9 mg/min/cm² as the nitric acid concentration was increased from 0.5 to 2.0 M.

Alternatively, decladding with mercury-catalyzed nitric acid was unsatisfactory because a mercury concentration of 0.5 M is required to assure an adequate dissolution rate. This is ~10 times the concentration normally required for aluminum dissolution. In 8 M HNO_3 -0.05 M $\text{Hg}(\text{NO}_3)_2$ titanium corroded at a maximum rate of 0.8 mil/mo in 456 hr exposure.

Graphite-Containing Fuel. By a grind leach process, >99.9% of the uranium was recovered from 5.5, 9.7, and 14.0 wt % uranium in graphite specimens. The samples were ground to -200 mesh and leached twice for 4 hr with boiling 15.8 M HNO_3 , and the residue was washed thoroughly with cold water. The iron content of these specimens varied from 0.07 to 0.4%. Only 99.7% of the uranium was recovered from a 11.2 wt % uranium fuel containing 0.8% iron.

Soxhlet extraction of plates of the General Atomics 1.5% uranium-7.1% thorium-graphite fuel with azeotropic nitric acid offered no advantages over a single leach with boiling 15.8 M HNO_3 , in which 10% of the uranium and thorium were insoluble.

Mechanical Processing. In tests to determine a satisfactory method of safely reacting the NaK released in SRE fuel decladding, reaction of NaK with steam was evaluated. The 98.4 ml contained in one fuel rod produced 1 liter of hydrogen per minute in reaction with steam at 0.4 lb/hr. Reaction was complete in 35 min.

In shearing-leaching tests the percent (P) of powdered UO_2 produced in shearing 0.4-in.-dia UO_2 -filled stainless steel tubes was related to the length of cut (L) by $P = 13/L^{1.22}$ for 0.5- to 5-in. lengths. In leaching tests it was demonstrated that stainless steel particles up to 1000 μ dia can be satisfactorily jetted from a batch dissolver.

Pilot Plant. The plant was on-stream 30 days during the month and a total of 12.5 metric tons of BNL irradiated uranium fuel containing 6.4 kg of plutonium was processed.

Operation of two extraction columns in the plant with the organic phase continuous resulted in a 10- and 3-fold increase in decontamination in the co-decontamination cycle and the final uranium cycle extraction columns, respectively. These changes eliminated the need of silica gel treatment for the final uranium product. Both uranium and plutonium products meet fission product specifications for subsequent processing. Based on measured losses from the plant, product recoveries for uranium and plutonium were 99.3 and 99.7%, respectively.

DISTRIBUTION

Internal

1. F. L. Culler
2. R. E. Blanco
3. J. O. Blomeke
4. F. R. Bruce
5. W. K. Eister
6. H. E. Goeller
7. A. T. Gresky
8. W. H. Lewis
9. M. J. Skinner
10. E. G. Struxness
- 11-13. ORNL Laboratory Records
14. ORNL-RC
- 15-16. Central Research Library
17. Document Reference Section

External

18. P. C. Aebersold, Washington AEC
19. B. Anderson, COO
20. E. L. Anderson, Washington AEC
21. F. P. Baranowski, Washington AEC
22. L. P. Bupp, HAPC
23. J. T. Christy, HOO
24. J. I. Hoffman, NBS
25. S. Lawroski, ANL
26. J. A. Lieberman, Washington AEC
27. B. Manowitz, BNL
28. R. B. Martin, OROO
29. J. W. Morris, SRP
30. E. E. Motta, AI
31. D. M. Paige, ICPP
32. J. L. Schwennesen, IDO
33. C. M. Slansky, ICPP
34. C. E. Stevenson, ICPP
35. W. B. Tarpley, Aeroprojects
36. L. Topper, NYOO
37. A. F. Voigt, ISC
38. F. M. Warzel, ICPP
39. T. R. Workinger, Washington AEC