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NON-PRODUCTION REACTOR FUELS REPROCESSING

AUTHOR

V. R. Cooper

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March 17, 1958

QUARTERLY REPORT

TECHNOLOGY FOR THE REPROCESSING OF NON-PRODUCTION REACTOR FUELS
BUDGET ACTIVITY 2790

By

V. R. Cooper

RESEARCH AND ENGINEERING OPERATION
CHEMICAL PROCESSING DEPARTMENT

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QUARTERLY REPORT

NON-PRODUCTION REACTOR FUELS REPROCESSING

This is the first in a series of quarterly reports on the research and development work carried out for Activity 2790 - Separations Development for Non-Production Reactors. Subsequent reports will be issued during March, June, September, and December.

By January, 1962, Hanford is to be prepared to process the fuel elements from the power reactors which employ depleted or slightly enriched uranium fuels. At the present time, Hanford is planning to process the fuel from the following reactors:

Reactor	Location	Designer
Yankee	Massachusetts	Westinghouse
Dresden	Illinois	General Electric
CPPD	Nebraska	North American Aviation
Piqua	Ohio	North American Aviation
Chugach	Alaska	Nuclear Development Corp.
PRDC	Michigan	Atomic Power Development Assoc.
Northern States	South Dakota	Allis-Chalmers

Conversion of the Uranium Recovery Plant to provide receiving and storage of power fuel elements, a mechanical handling operation, and the means of preparing a solution amenable to separation and decontamination by solvent extraction was visualized in the preliminary processing plans. The solution is to be transferred to the Redox Plant by pipeline. The plutonium nitrate is to be converted to buttons in the 234-5 Building and the uranium converted to UO_3 in the uranium conversion facility.

The fuel elements consist of uranium dioxide, uranium, or uranium alloy clad in aluminum, zirconium, or stainless steel. Either zirconium or stainless steel is resistant to chemical dissolution in media similar to any Hanford has used in the past. For this reason the principle effort to date on Activity 2790 has been directed toward the definition of flowsheets, equipment design and materials of construction required to convert the various elements into a solvent extraction feed.

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COORDINATION

Visit to Power Reactor Designers

Between January 13 and January 20, 1958, R. J. Sloat and R. E. Tomlinson visited:

Westinghouse, Pittsburgh, Pennsylvania

North American Aviation, Los Angeles, California

Allis Chalmers, Milwaukee, Wisconsin

General Electric, San Jose, California

Atomic Power Development Associates, Detroit, Michigan

Discussions were held with each company concerning the details of the power reactor fuel elements to be processed at H.A.P.O.

Shipping Cask Information

The following letters were submitted in reply to requests by the Atomic Energy Commission for preliminary concepts on standardized power fuels shipping casks:

W. K. MacCready to J. E. Travis, "Proposed Limitations for Shipping Casks for Power Reactor Fuels," February 5, 1958.

W. K. MacCready to A. T. Gifford, "Details on Handling of Spent Power Fuels," February 28, 1958.

MECHANICAL PROCESSING

Three approaches to mechanical processing of non-production fuels to permit core leaching are in the preliminary evaluation stage. These include sawing, shearing, and pulverizing. Circular sawing has been recommended by several equipment manufacturers as the best method for cutting jacketed fuel elements. Such a saw has been obtained and installation is 40 percent complete. Various sawing techniques and procedures will be evaluated by cutting simulated fuel elements composed of fused and sintered alkaline earth porcelain jacketed in zirconium or stainless steel. A carbide-tipped saw blade, a friction blade, abrasive wheels and diamond wheels will be tested.

CHEMICAL PROCESSING

Stainless Steel Jackets - Aqua Regia

One method of preparing a solvent extraction feed from non-production fuel elements jacketed in stainless steel consists of complete dissolution in aqua regia, 5 $\underline{M}$ HNO_3 - 2 $\underline{M}$ HCl. The Oak Ridge National Laboratory has obtained sufficient information to demonstrate process feasibility. Additional laboratory and pilot plant information are required to firm up flowsheets, materials of construction, and methods of chloride removal.

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Removal of Chloride From Dissolver Solution - Solvent Extraction

Batch studies were made to determine the requirements for removing chloride from aqua regia dissolver solution by solvent extraction. In this concept the dissolver solution composition would be adjusted and the solution would be fed to a Purex A-type column. The chloride would exit with the waste. The cost of extraction equipment and the neutralization and tanking of unconcentrated waste would have to be balanced against the cost of other chloride removal schemes and the value of decontamination obtained. After equilibration of a simulated solution (0.95 M UNH, 1.48 M HNO_3, 1.90 M HCl, SS dissolution products) with a two-volume portion of 30 per cent TBP in Shell E2342, the organic phase contained 5 g/l chloride and 97 g/l uranium. The results obtained with various scrubbing media are given below:

CHLORIDE REMOVAL
SCRUB STUDIES

Organic Phase: 5 g/l chloride, 97 g/l uranium
Organic to Scrub Volume Ratio: 5 to 1

Run No.	Scrub Composition	No. of Scrubs	Final Chloride Conc. in Organic, ppmp Uranium
1	3 M HNO_3, 16 g/l UNH	6	500
	Water	2	500
2	3 M HNO_3, 16 g/l UNH	6	-
	0.05 M $Cr(NO_3)_3$	3	15
3	3 M HNO_3, 0.03 M $Cr(NO_3)_3$, 16 g/l UNH	8	100
4	3 M HNO_3, 16 g/l UNH	6	-
	0.05 M $Al(NO_3)_3$	3	150
5	3 M HNO_3, 16 g/l UNH	6	-
	0.05 M $Fe(NO_3)_3$	3	>150
6	3 M HNO_3, 16 g/l UNH	6	-
	0.05 M $Hg(NO_3)_2$	3	>150
7	3 M HNO_3, 16 g/l UNH, 0.05 M $Al(NO_3)_3$	8	320

The data indicate chloride can be adequately removed by using chromium (III) in the scrub and that a dual scrub combination with the chromium only at the top of the column is preferable to a single scrub of chromium nitrate-nitric acid.

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Batch extraction, scrub and strip contacts were made on a synthetic Darex dissolver solution spiked with plutonium (IV) nitrate to the equivalent of about 500 grams plutonium per ton uranium. The plutonium exhibited normal TBP-process extraction and strip behavior.

Spectroscopic analysis of the extraction organic phase showed only a trace of iron and non-detectable amounts of chromium and nickel showing that the extracted chloride is not associated with stainless steel dissolution products.

Removal of Chloride from Dissolver Solution - Direct Boil Down

Optimum conditions (from the standpoint of time and nitric acid usage) for the removal of chloride by direct boil-down of dissolver solution involve initial concentration of the solution to a boiling point of about 130°C. Concentrated nitric acid (13 - 16 M) is then added contimuously and volatilized at the same rate as added. The solution is air sparged throughout the process. Chloride content of synthetic aqua regia dissolver solutions can be reduced from 68 g/l to about 0.1 g/l in a total operating time of about 10 hours. Fourteen to twenty moles of HNO_3 per liter of dissolver solution are used. Much of this acid could be used in subsequent dissolution or chloride removal procedures. Perfulfate and permanganate were found to accelerate chloride removal, but, because of large amounts required and probable subsequent processing difficulties introduced, their use is not considered promising.

In two runs in which the dissolver solution was spiked with radioactive ruthenium, about 20 percent of the ruthenium was volatilized.

Aqua Regia Dissolution Pilot Plant

Pilot plant equipment is being installed to demonstrate the aqua regia dissolution of stainless steel jacketed fuel elements. Initial experiments will be directed toward chloride removal by direct boil-down. The pilot plant will consist of a titanium dissolver. Vapors from the dissolver will pass through a titanium down-draft condenser. During dissolution, the condensate will return to the dissolver. During boil-down, condensate will be collected in a titanium acid receiver tank. Vapors passing the condenser will pass through a caustic scrubber before exhausted to the atmosphere. The installation is about 15 percent complete. The dissolver shell has been completed and most of the dissolver internal piping has been fabricated for installation.

Stainless Steel Jackets - HNO_3 - HF

An alternate process for the complete dissolution of stainless steel jacketed fuel elements involves the utilization of a mixture of nitric and hydrofluoric acid. It is possible that the material of construction for this vessel might be compatible with zirflex solutions. If this were the case, a single dissolution vessel would be capable of handling both stainless steel and zirconium jacketed elements.

Preliminary dissolution and corrosion rates are tabulated below. These are Huey-type tests and involve a one hour exposure of the metal to the boiling solution.

Dissolution Rates, Mils/Hr.

Solution	304-L	Haynes-25	Zircalloy-3
1) 5 M HNO_3, 1 M HF	1.03	0.055	85
2) 2 M HNO_3, 1 M HF	2.15	0.040	80
3) 1 M HNO_3, 1 M HF	4.00	0.050	70
4) 5 M HNO_3, 2 M HF	2.07	0.105	100
5) 2 M HNO_3, 2 M HF	4.75	0.120	100
6) 1 M HNO_3, 2 M HF	6.93	-	100

It is indicated that the dissolution of 304-L stainless steed (cladding material) in HNO_3 - HF systems can be carried out with a nitric acid concentration between 0.5 and 1.0 M and that satisfactory dissolution rates can be obtained at HF concentrations as low as 1 M.

Zirconium Jackets

The use of the zirflex process (aqueous ammonium fluoride dissolution medium) appears to be the most attractive method of removing zirconium jackets from non-production fuel elements. Laboratory work on this process is essentially complete, and most effort is being expended to determine equipment requirements by pilot plant scale studies.

Uranium and Zirconium Solubility in Zirflex Solutions

The solubility of uranium (IV) fluoride in boiling solutions of ammonium fluoride (of approximately six molar total fluoride) containing dissolved zirconium is given by the empirical expression

$$M_{U(IV)} = 6.9 \times 10^{-3} (M_{F-})^{1.4} + 2.9 \times 10^{-4}$$

where M_{F-} is the concentration of "free" fluoride defined as the total fluoride concentration minus six times the concentration of dissolved zirconium.

Measured zirconium fluoride solubilities in ammonium fluoride at 100 C and 22 C decreased markedly as the ratio of fluoride to zirconium increased, as expected from the fact that the salt $(NH_4)_3ZrF_7$ is less soluble than the salt $(NH_4)_2ZrF_6$. Solubilities measured at 22 C ranged from 1.19 M zirconium at a fluoride to zirconium ratio of 5.9 to 0.13 M at a fluoride to zirconium ratio of 21. Over a range of fluoride to zirconium ratios from 6.0 to 21 zirconium solubilities at 100 C varied from 3.2 M to 0.34 M.

The addition of ammonium nitrate to the ammonium fluoride appeared to decrease the solubility of both uranium(IV) and zirconium. There was no indication of oxidation of uranium(IV) on addition of ammonium nitrate to ammonium fluoride.

Zirflex Pilot Plant Studies

Pilot plant studies were initiated on the dissolution of zircaloy metal with aqueous ammonium fluoride solution. Experiments to date have employed 10 - 20 liters of boiling 6 $\underline{M}$ NH_4F - 0.5 $\underline{M}$ NH_4NO_3 to dissolve 1 to 1.5 kilograms of scrap zircaloy tubing or sheet metal. The studies have indicated:

(a) terminal dissolution rates of unoxidized metal which were lower than expected. (Recent studies suggest that this decrease in rate is due to the partial pressure of ammonia over the solution and can be avoided by sparging with air.)

(b) Production of copious quantities of "brown" (from the sheet metal) and "black" (from the tubing) precipitates.

(c) Very slow dissolution of the one metal charge which was deliberately subjected to oxidizing conditions.

MATERIALS OF CONSTRUCTION

Aqua-Regia System

A welded Haynes 25 coupon (no subsequent heat treatment) showed no visible preferential attack after exposure to 5 $\underline{M}$ HNO_3 - 2 $\underline{M}$ HCl for 200 hours. Weight loss measurements indicated a corrosion rate of about two mils/mo. However, after 300 hours exposure, severe preferential attack occurred in areas adjacent to the weld. In a similar test with Multimet alloy (cobalt-containing alloy stabilized with 1 percent niobium) preferential attack near the weld was even more severe. Corrosion rates of 4 and 18 mils/mo. were observed for titanium and Haynes 25, respectively, after exposure to 5 $\underline{M}$ HNO_3 - 2 $\underline{M}$ HCl under heat transfer conditions (metal temperature 135 C) for 240 hours.

Several non-metallic materials have been given static immersion tests at room temperature to determine their resistance to aqua regia. Conventional polyethylene, Super Dylan polyethylene, Marlex 50 polyethylene, Teflon, Kel-F, plasticized polyvinyl chloride, rigid polyvinyl chloride (Boltaron), Hypalon, and CSGBF graphite were tested in 2 $\underline{M}$ HCl - 5 $\underline{M}$ HNO_3. All showed excellent resistance. When these same materials were tested in 1 $\underline{M}$ HCl - 12 $\underline{M}$ HNO_3, the plastic polyvinyl chloride softened slightly but the other samples were essentially unaffected.

With the starting of construction of the pilot plant scale aqua regia dissolution equipment, a program was initiated to develop the required techniques for the welding of titanium. A cover for the dissolver was fabricated utilizing the inert-gas arc-welding process without the use of glove boxes. The resulting welds, although not silvery in appearance, were soft and ductile as evidenced by malleability and scratch tests. A gray deposit, assumed to be titanium oxide, observed on some of the welds caused concern as to their corrosion resistance. Laboratory tests showed no decrease (over unwelded titanium) in corrosion resistance to either aqua regia or 65 weight percent nitric acid.

Zirflex System

The corrosion rate (weight loss) of 304-L stainless steel exposed for 312 hours to 6 M NH_4HF under heat transfer conditions (metal temperature 135 C) was 1.6 mils/month. Numerous shallow pits were formed and penetrations as deep as 3 mils were observed. In a similar test with 4 M NH_4F - 0.5 M HF an apparent corrosion rate of 5.7 mils/month was observed. However, most of the corrosion occurred under a deposit of calcined salt along the edges of the test specimen. Pitting was not observed. Additional heat transfer tests, including the $NH_4F - (NH_4)_2ZrF_6 - NH_4NO_3$ system are in progress.

A corrosion rate of 0.1 mil/month was observed for a 304-L coupon half submerged in boiling 4 M NH_4F. Shallow pits were observed beneath a heavy scale which formed at the interface.

Data from Huey-type corrosion tests of 304-L stainless steel, by solutions simulating those remaining after a zirflex decladding step and subsequent dissolution of uranium in HNO_3 - $Al(NO_3)_3$ and without a metathesis step, have indicated satisfactorily low corrosion rates. Results of similar tests under heat transfer conditions (metal temperature 140 C) are tabulated below:

Solution	Corrosion Rate, Mils/Mo.
12 M HNO_3 - 0.5 M $Al(NO_3)_3$ - 0.02 M UNH - 0.08 M HF	4.4
12 M HNO_3 - 0.5 M $Al(NO_3)_3$ - 0.02 M UNH - 0.16 M HF	7.1
6 M HNO_3 - 0.06 M $Al(NO_3)_3$ - 1.0 M UNH - 0.08 M HF	1.2

These rates are not considered excessive since the high acid conditions will exist for short times only. The corrosion was largely intergranular.

In Huey-type tests, low carbon Hastelloy F showed corrosion rates of less than 0.05 mils/mo. in boiling solutions of 4 M NH_4F, 4 M NH_4F - 0.5 M NH_4NO_3, 1 M $(NH_4)_2ZrF_6$, 10% NaOH - 20% $NaNO_3$, and synthetic Redox coating removal waste. Corrosion rates in boiling 60 and 40% HNO_3 were about 1.2 and 0.4 mils/mo., respectively. Data to date on the resistance of low carbon Hastelloy-F to Zirflex dissolver solutions under heat transfer conditions are erratic with respect to both general attack and pitting. Further tests are in progress.

HNO_3 - HF System

Corrosion rates for 309 SCb stainless steel, Haynes 25, and Hastelloy F and X alloys in HNO_3 - HF systems were obtained. Hastelloy X and 309 SCb had prohibitively high corrosion rates. Haynes 25 showed satisfactory resistance to attack when completely annealed. When heated to 1200 F and water quenched corrosion was increased and "as welded" coupons showed severe attack in areas adjacent to the weld.

Attention was concentrated on Hastelloy F because of its unusually good resistance to HNO_3 - HF solutions. Hastelloy-F containing low carbon (ca. 0.01%) corrodes at about 2 mils/mo. in boiling 1 M HNO_3 - 2 M HF with no indication of preferential attack; with intermediate carbon content (0.04%), intergranular corrosion is serious; and at high carbon (0.08%), the metal is also subject to severe sensitization during welding. Attempts are being made to obtain samples of low carbon base metal welded with low-carbon metal. Weld sensitization in such specimens will be studied to determine if post-welding heat treatment is necessary. Corrosion rates for low carbon Hastelloy-F in 1 M HNO_3 - 2 M HF under heat transfer conditions (metal temperature 125 - 135 C) were about five mils/mo. and no preferential attack was observed.

EQUIPMENT DEVELOPMENT

Titanium Valve Development

Initial testing of an all-titanium control valve (nominal 1 gpm) for possible use in an aqua regia system has indicated the basic operability and feasibility of the solenoid-type valve.

ANALYTICAL TECHNIQUES

Investigation of Methods for Determining Chloride Ion Concentration in Darex Process Solutions

Laboratory studies directed toward a suitable potentiometric method for determining chloride ion concentration in Darex process solutions are continuing. The two systems (1) calomel reference electrode, calomel detecting electrode, and (2) silver-silver chloride reference, silver-silver chloride detecting electrode, yield non-reproducible results. The calomel detecting electrode is unsatisfactory in that the mercurous chloride adsorbs solution and has a "memory" and thus fails to detect changes in chloride ion concentration. The system of two silver-silver chloride electrodes gives very poor results under the conditions of the experiment. A calomel reference electrode with a silver-silver chloride detecting electrode exhibits excellent stability and reproducibility. Voltage readings have held constant for five days, and the system responds immediately to changes in chloride ion concentration. The logarithm of the chloride ion concentration is a linear function of the measured voltage from 1 M to 10^{-5} M chloride ion. The measured voltage changes 50 millivolts for a ten-fold change in chloride ion concentration.

Work is now directed towards determining the life of the electrode in various concentrations of nitric acid.

CRITICALITY STUDIES

The preparation of approximately 600 pounds of $UO_2(NO_3)_2 \cdot 4H_2O$ at 2.10% U_{235} enrichment is in progress. This comprises the material needed for the first part of a criticality experiment to determine K_{∞} for several homogeneous systems of enriched uranyl nitrate and water.