IN-1069
March 1967

MASTER

LABORATORY FEASIBILITY STUDIES
OF AQUEOUS REPROCESSING
OF ZIRCONIUM DIOXIDE-URANIUM DIOXIDE FUELS

R. G. Butzman and B. J. Newby

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

IDAHO NUCLEAR CORPORATION
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Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

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H.C. \$300; MN 65

IN-1069

Issued: March 1967

Chemical Separations Processes
for Plutonium and Uranium

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U. S. Atomic Energy Commission Research and Development Report
Issued Under Contract AT(10-1)-1230
Idaho Operations Office

A B S T R A C T

A three-step batch dissolution process for Zircaloy-clad zirconium dioxide-uranium dioxide fuels (such as PWR Core 2 Seed 1) using aqueous hydrofluoric acid and chromic acid solutions is proposed, and a chemical-flowsheet is given with supporting data.

SUMMARY

The fuel elements of the first seed of the second core of the Pressurized Water Reactor (PWR) at Shippingport, Pennsylvania, are composed of sintered wafers of fully enriched uranium dioxide (28%) zirconium dioxide (72%) clad with Zircaloy-4. A technically feasible method for dissolving this fuel consists of the following three consecutive batch operations: (1) decladding in 5M hydrofluoric acid-0.1M potassium fluoride; (2) dissolving the zirconium dioxide from the meat and converting the uranium dioxide to uranium tetrafluoride with 20M hydrofluoric acid-0.05M potassium fluoride; and (3) dissolving the uranium tetrafluoride in 0.1M chromic acid. Uranium losses to the waste streams from steps (1) and (2) are about 0.1%. Monel, which is the material of construction of the existing Idaho Chemical Processing Plant (ICPP) dissolver for zirconium fuel, is suitable for the proposed process, and modest production rates appear possible with essentially the present dissolver configuration. The product solution from dissolution is readily adjusted for solvent extraction of uranium in existing ICPP equipment.

Limited investigation of uranium dioxide-zirconium dioxide-calcium oxide wafers, using this flowsheet, has shown that wafers containing calcium oxide dissolve about one-tenth as rapidly as those composed of uranium dioxide and zirconium dioxide only. This very slow dissolution rate makes this approach extremely unattractive for fuels containing calcium oxide.

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I. INTRODUCTION

The fuel elements of Seed 1 of Core 2 of the Shippingport Pressurized Water Reactor consist of sintered wafers of fully enriched uranium dioxide-zirconium dioxide clad with Zircaloy-4⁽¹⁾. For purposes of preparing the chemical flowsheet, the uranium dioxide-zirconium dioxide wafers have been estimated to represent about 22 weight percent of the fuel, and the uranium dioxide content of the wafers to be about 28 weight percent. Later, when more exact original compositions, burnups, and the degree of mechanical disassembly prior to dissolution are known, a more exact material balance can be prepared. No calcium oxide is present. These elements are assembled into subassemblies and assemblies of a configuration similar to that of Core 1, although the assemblies are generally larger in size⁽²⁾. The ICPP already has high-capacity facilities for the dissolution and solvent extraction of the fuel from the seeds of Core 1 of the PWR⁽³⁾, and it has appeared desirable to determine if the seeds from Core 2 could be processed in identical or slightly modified facilities. This report summarizes the early development work for an aqueous recovery process for the enriched uranium in this fuel and presents a reference chemical flowsheet for a feasible, but not necessarily optimum, process.

Based on preliminary dissolution rate measurements, the properties of zirconium fluoride-uranium tetrafluoride and related solutions, and the available corrosion data for these solutions, it was apparent that a homogeneous batch or continuous dissolution could not be accomplished with this fuel in a fluoride system, and a fluoride system is the only aqueous system which could be useful for dissolving the zirconium dioxide-uranium dioxide wafers. Because there is a difference of about three orders of magnitude in the rates of dissolution of zirconium dioxide and Zircaloy-4 in aqueous fluoride reagents, it is essentially impossible to select a composition that will give a safe rate of reaction with the Zircaloy-4 cladding, and still give an adequately rapid rate of reaction with the wafers. Additionally, the solubility of uranium tetrafluoride in the zirconium fluoride solutions is too low to yield a completely homogeneous solution with this fuel composition, at any reasonably high concentration of zirconium. These factors all suggest the multi-step dissolution procedure which is described in the body of this report.

II. CHEMICAL FLOWSHEET FOR PROPOSED PROCESS

The preliminary development data for the dissolution of this fuel suggested a three-step dissolution process which appears to be technically feasible, with reagents compatible with the materials of construction of existing vessels at ICPP. This yields, with adjustment, a solvent extraction feed stream which is compatible with existing solvent extraction practices and equipment. The chemical process flowsheet is shown in Figure 1. The three steps required for the dissolution of the fuel are:

decladding, dissolution of the zirconium dioxide, and dissolution of the remaining uranium tetrafluoride. Boric acid may be present in any or all of the three reagents if required for criticality control. The various steps projected for the process flowsheet are described in the following sections.

1. Fuel Charging

The chemistry of the process, as currently envisioned, places no restrictions on the geometry of the fuel, or the batch size. Considerations of criticality and economics dictate the extent of prior mechanical removal of structural material, the geometry of the dissolver, and the amount of charge. For the purposes of this flowsheet, a fuel charge of one kilogram is considered with quantities of zirconium, zirconium dioxide, and uranium dioxide distributed according to the earlier description of the fuel. All operations are performed batchwise.

2. Decladding

It is highly desirable to perform a clean decladding operation on this fuel to avoid the necessity of processing for uranium recovery the zirconium fluoride solution originating from the cladding. Decladding and partial dissolution of the massive structural pieces of Zircaloy on the element are done with 5M hydrofluoric acid at about 70°C. Potassium fluoride is present in the solution to permit formation of the highly insoluble double salt with uranium fluoride in the event that any uranium dioxide dissolves during the decladding operation. Decladding is complete in about 15 minutes with approximately 60 percent of the total Zircaloy in cladding and structure dissolved. The decladding waste solution is decanted from the wafers of zirconium dioxide-uranium dioxide and Zircaloy residue.

3. Dissolution of the Zirconium Dioxide

It would be advantageous to leach the zirconium from the zirconium dioxide-uranium dioxide wafers without dissolving uranium, thus avoiding the necessity of having to process the resulting zirconium fluoride solution for uranium recovery. To accomplish this, the zirconium dioxide from the wafers, and additional Zircaloy from the fuel element structure, is dissolved in 20M hydrofluoric acid in about 2½ hours at the boiling point. The thin layer of pyrolytic carbon which covers the compact is disintegrated, but not dissolved, in this step. As during decladding, potassium fluoride is present to reduce uranium solubility. During this treatment the uranium dioxide of the fuel is converted to uranium tetrafluoride. The highly insoluble three-quarter hydrate has been identified specifically in the solids. At this point the zirconium dissolvent solution is decanted from the uranium tetrafluoride residue. The development work completed to date indicates uranium losses to the combined waste streams to be less than 0.1 percent, with most of this in the waste stream from wafer dissolution.

Fig. 1 Reference Flowsheet for PWR Core 2 Seed 1 Fuel

4. Dissolution of Uranium

The uranium tetrafluoride residue dissolves readily in 0.1M chromic acid at the boiling point in $2\frac{1}{2}$ hours. In the course of dissolution the uranium is oxidized to uranyl ion and is thus in the proper valence state for solvent extraction with tributyl phosphate.

5. Adjustment and Solvent Extraction

The dissolver product solution is adjusted with 6M nitric acid-0.4M aluminum nitrate solution to yield a feed stream for the extraction column which is essentially nitric acid solution. The small amount of fluoride carried over is more than amply complexed by the aluminum and will not have a significant effect on the extraction of uranium or corrosion of equipment. The chromic acid presumably will decompose slowly, but if it causes any undesirable effects at this point it may be destroyed by the use of a mild reducing agent. The volume of the raffinate from the first cycle extraction system is about 880 liters per kg of uranium, a value that compares very favorably with that for other flowsheets for reprocessing enriched uranium fuels.

There are no features of the solvent extraction flowsheet which require new supporting data. Existing distribution data for uranium ⁽⁴⁾ indicate that a distribution coefficient of about 20 will be obtained in the extraction column. Other aspects of the flowsheet are also conventional.

6. Waste Processing

The zirconium waste from the cladding will be blended with the zirconium waste from the fuel wafers, and this mixture will be blended with the first-cycle solvent extraction raffinate from this process or with other aluminum containing raffinates; the resultant mixture will be calcined to a free-flowing solid ⁽⁵⁾. The feasibility of processing zirconium fluoride wastes with minimum modification of the Waste Calcining Facility (WCF) has been proven in a pilot run made in a twelve-inch-diameter calciner. Greater than 99 percent of the potentially volatile fluoride in the waste was retained in the solids by reacting the fluoride with a stoichiometric amount of calcium. Corrosion data indicated that the austenitic stainless steels from which the WCF is constructed are satisfactory in calcination service. Only trace amounts of fluoride were volatilized from the solid product when it was heated at 800°C, indicating that the calcium-zirconium-fluoride compounds that are formed will be stable during storage up to that temperature.

Because the uranium dioxide will be completely converted to uranium tetrafluoride during the dissolution of the zirconium dioxide, there will be a split of the fission products between the zirconium waste from the fuel wafers and the first cycle solvent extraction raffinate. Very likely each will be a high activity level waste and probably will have to be treated as such. The zirconium waste from the cladding, in contrast, will certainly be a moderate level waste, and could be treated separately if that were more economical.

7. Materials of Construction

All of the reagent and product streams used in the dissolution are compatible with Monel, the material of choice for hydrofluoric acid solutions. The adjustment vessels can be Carpenter-20, and the solvent extraction equipment can be made of Type 304 stainless steel. These materials are now used in similar service at ICPP (3). The waste evaporator should be Monel, and the tanks holding uncomplexed fluoride solutions can be made of either Carpenter-20 or Monel. Type 304 stainless steel, or its equivalent, appears to be adequate for long term storage of complexed fluoride containing solutions such as the blended waste (6). Present indications are that the materials of construction of the Waste Calcining Facility, primarily stainless steels, are satisfactory for the calcination of adequately complexed fluoride containing solutions (7).

8. General Observations

The chemical flowsheet presented in Figure 1 appears to be technically feasible for the dissolution of PWR Core 2 Seed 1, for the adjustment of the solution for solvent extraction, and for the partial processing of the various wastes. Recovery of uranium following this headend would be entirely conventional. It is presented at this time as the reference flowsheet for the process, with the assumption that at least minor improvements will be made in it as development work proceeds.

III. SUPPORTING DATA FOR THE THREE-STEP DISSOLUTION PROCESS

1. Scoping Studies

1.1 Decladding

The compacts of uranium dioxide-zirconium dioxide in this fuel are not completely inert in dilute hydrofluoric acid, although the rate of attack is very slow. By using 5M hydrofluoric acid-0.1M potassium fluoride solution (11 ml/g of fuel), controlling the temperature at 70°C, and limiting the contact time to about 15 minutes, it is possible to obtain decladding with very low uranium losses to the decladding waste solution. Data from experiments with varying levels of potassium fluoride at two temperatures are shown in Table I and Figure 2. These illustrate the generally low losses possible in decladding and the advantages of lower temperature and of having a small concentration of potassium fluoride present to allow formation of the less soluble double salts with uranium fluoride in solution.

1.2 Leaching of Zirconium from the Meat

When zirconium dioxide-uranium dioxide meat is boiled with 20M hydrofluoric acid solution, the zirconium dioxide is dissolved and the uranium dioxide is converted to $UF_4 \cdot 3/4 H_2O$ in situ. That is, the wafers that were initially composed of zirconium

Table I
DECLADDING OF PWR CORE 2 SEED 1
Reagent: 5M HF + KF

<u>KF</u> <u>M</u>	<u>Zr from Cladding</u> <u>M</u>		<u>Uranium Loss to</u> <u>Decladding Solution</u> <u>%</u>	
	<u>15 min</u> <u>at 70°C</u>	<u>60 min</u> <u>at 96°C</u>	<u>15 min</u> <u>at 70°C</u>	<u>60 min</u> <u>at 96°C</u>
0.0	--	0.78	--	0.57
0.0	0.79*	--	0.06*	--
0.05	0.78	0.90	0.04	0.68
0.09	0.70	0.78	0.02	0.49
0.125	0.65	0.68	0.009	0.30

* 0.09% U loss at 60 minutes at 70°C.

dioxide-uranium dioxide become porous wafers of $UF_{4.3/4}H_2O$ during the digestion with 20M hydrofluoric acid. In Figure 3, wafer pieces at A are ZrO_2-UO_2 , those at B are $UF_{4.3/4}H_2O$. Decreasing the hydrofluoric acid concentration below 15-20M decreases the dissolution rate of zirconium oxide from the mixed oxide compacts to an unacceptably low level. (9,8) During the dissolution of zirconium oxide from the mixed oxide wafers with 20M hydrofluoric acid solution, some of the uranium dissolves. The data given in Table II (p. 9) show that the addition of potassium fluoride to the leaching solution keeps uranium losses to the solution at an acceptably low level. The data in Table II also indicate: (a) that the percent of uranium dissolved is independent of potassium fluoride concentration over the range 0.05 to 0.125M and independent of the time that the solutions are boiled; and (b) that 2.5 hours of boiling time should be adequate to dissolve essentially all of the zirconium oxide from the mixed oxide compact. The dissolutions summarized in Table II were carried out in a Monel dissolver with 1.0 scfh of nitrogen bubbling through the solution during dissolution (to reduce Monel corrosion), and using 106 ml of hydrofluoric acid solution per gram of compact. In the dissolution using potassium fluoride, the leaching solution was boiled with the compact for 2.5 hours and then allowed to stand at 24°C for 21.5 additional hours with the compact. In dissolutions not using potassium fluoride, the leaching solution was boiled with the compact for two hours.

Fig. 2 Uranium Losses During Decladding of PWR Core 2 Seed 1 Fuel

Fig. 3 Declad PWR Core 2 Seed 1 Wafers; Before (A) and After (B) ZrO_2 Dissolution Step

1.3 Dissolution of Uranium from the Meat

Two experiments were performed in which 0.1M chromic acid solutions were used to dissolve the $\text{UF}_4 \cdot 3/4\text{H}_2\text{O}$ residue remaining after uranium dioxide-zirconium dioxide meat had been boiled with 20M hydrofluoric acid solution. In both experiments a volume of chromic acid solution was used equal to the volume of 20M hydrofluoric acid solution used to attack the meat in the preceding step. In one experiment, 0.1M chromic acid was used as dissolvent; in the other, 0.1M chromic acid-0.37M boric acid was used. All visible residue dissolved after being boiled in the chromic acid solutions for about $2\frac{1}{2}$ hours.

2. Confirmatory Dissolution Studies

2.1 Equipment and Procedure

For further evaluation of the proposed flowsheet for PWR Core 2, Seed 1 fuel dissolution, a laboratory-scale dissolver was constructed with about 1/1000 the working volume of the plant dissolver (ICPP vessel E-101). An attempt was made to have the laboratory dissolver, as much as possible, be a small scale representation of the plant dissolver. A fuel basket was employed in the laboratory vessel, along with a thermocouple well, one nitrogen sparge line, and one line for introducing and removing solution. (The plant vessel contains a number of lines for transferring

Table II

LEACHING OF ZIRCONIUM FROM THE MEAT OF PWR CORE 2 SEED 1
 WITH 20M HF + 0.37M H_3BO_3 + KF

Temperature °C	KF M	Zr from Meat M					% U Loss to Leach Solution				
		<u>1 hr</u>	<u>1.5 hr</u>	<u>2 hr</u>	<u>2.5 hr</u>	<u>21.5 hr</u>	<u>1 hr</u>	<u>1.5 hr</u>	<u>2 hr</u>	<u>2.5 hr</u>	<u>21.5 hr</u>
96	0	--	--	0.067	--	--	--	--	0.2	--	--
96	0	--	--	0.060	--	--	--	--	0.23	--	--
96	0.05	0.05	0.05	0.05	.047	--	0.05	0.05	0.05	0.01	--
24	0.05	--	--	--	--	0.056	--	--	--	--	0.02
96	0.09	0.033	0.041	0.050	0.058	--	0.03	0.03	0.03	0.05	--
24	0.09	--	--	--	--	0.059	--	--	--	--	0.02
96	0.125	--	0.041	0.046	0.050	--	--	0.03	0.03	0.03	--

liquid, as well as several instrument lines.) The laboratory vessel was $3\frac{1}{2}$ inches ID and 12 inches deep and could accommodate up to 1200 ml of solution with adequate head space. The bolt-on cover was equipped with a reflux condenser to minimize hydrofluoric acid vapor losses. This dissolver was made of Monel and is shown in Figure 4.

A number of dissolutions with unirradiated fuel pieces were performed in this equipment following the proposed flowsheet. All of these dissolutions were performed under a nitrogen atmosphere for two reasons: The exclusion of oxygen is necessary to minimize the corrosion rate of Monel in hydrofluoric acid medium; secondly, oxygen in solution causes insoluble $\text{UF}_4 \cdot 3/4\text{H}_2\text{O}$ to be oxidized to soluble UO_2F_2 . It was arbitrarily decided to maintain the oxygen level at one percent or less whenever reagent was present in the dissolver. (The nitrogen flow was maintained continuously at 1000 ± 200 cc/min throughout the course of each run to keep the vessel purged of oxygen and to provide some mixing action.)

2.2 Experimental Results

2.21 Uranium Losses: Of particular interest during the confirmatory runs were the uranium losses to the two waste streams. Table III lists the uranium losses for four of the runs made in the laboratory scale dissolver. It was concluded that due to the physical configuration of the uranium tetrafluoride wafers, solid macro uranium tetrafluoride was not being carried out of the dissolver with the exiting dissolvent. In addition, several of the zirconium waste solutions from fuel wafers (which are greenish in color, resembling a suspension of $\text{UF}_4 \cdot 3/4\text{H}_2\text{O}$) were examined for a Tyndall effect and none was observed. One batch of this solution was analyzed in such a manner so as to differentiate between U^{+6} and U^{+4} . There was no significant amount of U^{+4} present. It was concluded that the uranium losses were not due to colloidal or soluble uranium tetrafluoride, but rather to the small amount of uranyl ion produced by oxygen or oxidants entering the dissolver.

2.22 Dissolution of Irradiated Fuel: A single experimental run was made on a sample of irradiated fuel, representative of PWR Core 2 Seed 1 fuel. The burnup was about 45 percent. This material was dissolved remotely in the Monel laboratory scale dissolver using the proposed flowsheet. Essentially complete dissolution was achieved. The total uranium loss to the waste streams was 0.62 percent, which is greater than the total loss with unirradiated fuel. No explanation is available from this single experiment as to why this occurred.

2.23 Effect of Calcium Oxide in the Ceramic Wafer: Future seeds of PWR-2 may contain meat that consists of uranium dioxide-zirconium dioxide, plus calcium oxide. A comparative

Fig. 4 Partially Disassembled Laboratory Dissolver Showing Internal Components

dissolution test was performed on PWR Core 2, Seed 1 declad wafers and on declad wafers containing approximately two percent calcium oxide, as estimated by emission spectroscopy. These tests were done in Teflon-ware with each type of fuel subjected to identical dissolving conditions; ie, 100 times the stoichiometric amount of 20M hydrofluoric acid-0.05M potassium fluoride at boiling. The dissolution rate curves appearing in Figure 5 were drawn from the zirconium analyses of the samples of dissolver product solution taken periodically during the dissolution reaction for each type of meat.

The constants in the parabolic rate expression

$$C_{Zr}^2 = kt$$

were 1×10^{-5} and 1×10^{-6} (moles²/liter²-min) for calcium-free meat and meat containing approximately two percent calcium oxide, respectively. A feasible, high capacity process in this dissolvent could not be developed for the calcium oxide containing fuel due to this slow dissolution rate.

2.3 Corrosion Evaluation of Dissolver

In order to get some impression of the corrosive effects of the process solutions on Monel, weight losses were measured on the laboratory scale dissolver and its components, individually, over the course of several experimental runs. The cover was the only item that experienced uniform exposure, ie, the same amount of area of the cover was exposed to vapors only for each run. In the case of the dissolver and the hardware contained in it, each piece was exposed intermittently to both vapors and liquid. The liquid depth varied from a maximum of eight inches to a minimum of one inch. A height of nine inches was selected for calculating the exposed areas for the dissolver, the fuel basket, the nitrogen sparge line

Table III

URANIUM LOSSES TO THE WASTE STREAMS

Run No.	Uranium Expressed as Percent of Total Present in System		
	In Zirconium Waste from Cladding	In Zirconium Waste from Fuel Wafers	Total Loss
A	0.012	0.055	0.067
B	0.008	0.038	0.046
C	0.074	0.001	0.075
D	0.090	0.0004	0.090

Fig. 5

Comparative Dissolution Rate Curves
for PWR Wafers with and without Calcium Oxide

and the liquid transfer line; all of the individual weight losses were assigned to those areas. The corrosion measurements are listed in Table IV.

Table IV

CORROSION RATES EXPERIENCED IN THE LABORATORY SCALE MONEL DISSOLVER

<u>Equipment Component</u>	<u>Type of Exposure</u>	<u>Corrosion Rate (mils/month)</u>
Cover	vapors	4
Vessel	solution, vapor	12
Fuel Basket	solution, vapor	8
Sparge Line	solution, vapor	18
Liquid Transfer Line	solution, vapor	12

These preliminary corrosion measurements suggest that this flowsheet will result in a relatively high rate of attack on Monel. Alternating exposure to hydrofluoric and chromic acids is more corrosive than either reagent individually. Analyses have shown that the 20M HF preferentially dissolves nickel. The chromic acid attacks both components of the alloy so there is no chance for passivation of the Monel to occur.

However, high corrosion rates are characteristic of the processes for zirconium clad fuels. The batch Monel dissolver at ICPP suffered a corrosion rate of 5.8 MPM over a period of 1078 operating hours during the processing of zirconium-uranium alloy fuels. (10) These relatively high corrosion rates do not preclude the use of the flowsheet and vessel where the fuel available for reprocessing requires only short operating times.

IV. CONCLUSIONS

It appears technically feasible to process Zircaloy-clad zirconium dioxide-uranium dioxide fuel by an all-aqueous method in a three-step batch dissolution process. The proposed method for processing this type of fuel can be readily adapted to existing ICPP dissolution, solvent extraction, and waste processing equipment. A reference flowsheet for the processing of advanced PWR fuel is presented which includes suggestions for dissolution, solvent extraction, and raffinate processing. This flowsheet may not be optimum, but it will serve as a reference for evaluation of the additional development work on the process which is now in progress. The presence of calcium oxide in a fuel of this type will have an adverse effect on the rate of dissolution in aqueous fluoride media.

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