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AN IMPROVED AQUEOUS PROCESS FOR
ZIRCONIUM ALLOY NUCLEAR REACTOR FUELS
PART 1. PRELIMINARY LABORATORY STUDIES

K. L. Rohde, et al

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US ATOMIC ENERGY COMMISSION

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B. J. Newby	T. L. Hoffman
B. E. Paige	L. A. Decker

(K. L. Rohde, Editor)

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A B S T R A C T

The expanding use of Zircaloy-clad zirconium-enriched uranium alloy fuel has suggested a need for higher capacity reprocessing facilities. The most urgent requirement is for continuous dissolution equipment to match the solvent extraction capacity already available at Idaho Chemical Processing Plant. Because of the rapid dissolution rates possible with aqueous hydrofluoric acid on clean metal as well as on oxidized fuels, and subsequent flowsheet economics, it is the reagent of choice.

Laboratory measurements and a survey of the properties of uranium tetrafluoride indicated highest solubility in the dissolver effluent was obtained at higher total fluoride concentrations and lower fluoride-to-zirconium mole ratios. Since zirconium salts have been shown to be susceptible to precipitation at higher fluoride and zirconium concentrations, an optimum dissolver effluent composition was selected for a Dilute Flowsheet at about 5M total fluoride and a 1.1M zirconium.

The operation of two bench-scale dissolvers verified the feasibility of a continuous process, and Monel and Carpenter-20(Cb) were confirmed as suitable materials of construction for the dissolver. Using the Dilute Flowsheet, uranium solubility equivalent to the dissolution of fuels containing 2 per cent uranium, over-all, was achieved.

Correlations of dissolver effluent flow rate with effluent composition and with total zirconium dissolved are given for guidance in engineering scale-up.

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AN IMPROVED AQUEOUS PROCESS FOR ZIRCONIUM ALLOY NUCLEAR REACTOR FUELS

PART I. PRELIMINARY LABORATORY STUDIES

I. SUMMARY

The continued acceptance of Zircaloy-clad zirconium-uranium alloy fuels for military propulsion reactors has suggested that a high capacity process for the recovery of the fully enriched uranium fuel from this source would be required. Since a high capacity solvent extraction system is already available at the Idaho Chemical Processing Plant, the primary equipment and process need for greater zirconium fuel reprocessing rates is a continuous dissolver. The well-established hydrofluoric acid dissolution process and its associated solvent extraction flowsheet are preferred over other aqueous processes for this fuel.(14)

For the development of the chemical flowsheet for continuous dissolution, new kinetic data for the reaction of Zircaloy-2 and zirconium with hydrofluoric acid and the fluozirconic acids of the dissolver product solution were obtained. The reaction of fuel with oxidized surfaces was initiated and sustained in hydrofluoric acid at 30°C or higher. At fluoride-to-zirconium mole ratios greater than 7 and total fluoride concentrations greater than 6M a rate constant of 61 mg cm⁻² min⁻¹ per mole HF liter⁻¹ was observed for the dissolution reaction. At a mole ratio of 5 and a total fluoride concentration of 5.3M (a composition very close to the preferred dissolver effluent) the rate was 12 mg cm⁻² min⁻¹. Studies of the solubility of uranium tetrafluoride in the dissolver product solution indicated that a Dilute Flowsheet, about 5M total fluoride and 1.1M zirconium, would lead to the required uranium solubility without sacrificing any addition in ultimate waste storage bulk.

Data on the operational behavior of dissolvers, the effect of reagent flow rate on effluent composition, and certain scale-up correlations were obtained from the operation of two bench scale dissolvers. The dissolver "loading curve" (variation in effluent composition with reagent flow rate) is exceptionally flat. A change in effluent flow rate-to-fuel surface area ratio from 0.03 to 0.3 cm per min results in a decrease in concentration from 1.25 to 1.14M zirconium in the effluent. In effect, the dissolver is self controlling. The dissolver production (moles of zirconium dissolved per hr-in² of dissolver cross section) varies as the 0.94 power of the reagent flow (moles of fluoride per hr-in²) between 2 and 50 moles of fluoride per hr-in². The dissolution

rate of Zircaloy-2 in the reagent is about 300 mg per $\text{cm}^2\text{-min}$. In the bench scale continuous dissolver rates between 4 and 30 mg per $\text{cm}^2\text{-min}$ were realized depending on the reagent flow rate.

Analysis of the dissolver effluent verified the trend in uranium solubility observed in basic solubility studies. The uranium solubility increased with decreasing fluoride-to-zirconium mole ratio and with increasing total fluoride concentration. The homogeneous dissolution of fuels containing 2 per cent uranium over-all was indicated.

The corrosion resistance of both Monel and Carpenter-20(Cb) was tested, the former being preferred because of the difficulty in obtaining good field annealing after welding of the latter. Active oxidizing substances, such as nitric acid, which might be introduced into the chemical flowsheet were shown to be corrosive to Monel and their concentration must be carefully limited.

Further studies are required to define the process chemistry of uranium more closely, verify the performance of Monel as the material of construction, and secure additional data on continuous dissolver operation.

II. INTRODUCTION

The increasing use of Zircaloy-clad zirconium-uranium alloy fuels for military propulsion reactors⁽¹⁾ indicates that a higher capacity process for the recovery of the enriched uranium from this source than is presently available at the Idaho Chemical Processing Plant would be required. The existing process equipment,⁽²⁾ which was designed for the batch dissolution and low-capacity solvent extraction of the fuel, has been operated effectively,^(3,4) but at very low, and therefore, uneconomic throughputs. The chemistry of the hydrofluoric acid dissolution process also imposes some limitations on the application of the process to fuels which contain higher ratios of uranium to zirconium. Additionally, the column feed and raffinate has a relatively high specific volume after being complexed with aluminum nitrate, which results in high costs for aqueous waste storage. Although a number of other methods have been designed to process this same type of fuel, these have not appeared competitive for immediate application, primarily because they involved various aspects of high temperature technology. Also, none of these have come to the same level of development as the aqueous hydrofluoric acid process.

Since a high capacity solvent extraction system is available in the Idaho Chemical Processing Plant (ICPP), the primary equipment need for higher zirconium fuel production is either a number of batch dissolvers or a high capacity continuous dissolver. The inherent economic advantages of the continuous dissolution system, and the successful experience with the continuous dissolvers for aluminum fuel at ICPP⁽⁵⁾, strongly suggested that a continuous dissolution process should be developed for the zirconium alloy fuels. Since homogeneous process

and waste solutions are a design philosophy at ICPP, flowsheet chemistry studies had to be directed toward the development of methods for insuring the solubility of the uranium from fuels containing 2 to 3 per cent uranium, over-all, in the chemical system where the solubility of uranium tetrafluoride was very limited. Vigorous oxidation of the uranium to the hexavalent state in the dissolver could not be tolerated because of the corrosion sensitivity of the materials of construction.

Laboratory studies of batch dissolution had shown that the use of low concentrations of oxidizing agents (hydrogen peroxide, nitric acid, chromic acid, potassium permanganate)⁽⁶⁾ and the use of a dissolver product solution dilute with respect to zirconium concentration,⁽⁶⁾ all favored the homogeneous dissolution of fuels containing higher percentages of uranium. The enhancement of solubility by oxidation was recognized as being potentially radically different when done under batch and continuous dissolving conditions. In the batch dissolution it was entirely conceivable that the oxidation-dissolution of a portion of the uranium tetrafluoride took place after the zirconium dissolution was essentially complete. In a continuous dissolver, operated on a single region principle, it is difficult to visualize the simultaneous dissolution of zirconium, with the reduction of hydrogen ion, and oxidation of uranium to uranyl ion. Therefore it was particularly important to establish the value of oxidants under continuous dissolution conditions.

The Dilute Flowsheet, which uses no significant amount of oxidant was based on fundamental solubility measurements,⁽⁷⁾ and has been proven suitable for fuels up to 2 per cent uranium, over-all, in laboratory batch dissolutions.⁽⁶⁾ Because no corrosion problems are associated with this flowsheet it is particularly important to verify its application in continuous dissolution.

The dissolution of uranium-zirconium alloy clad with Zircaloy-2 can lead to three different types of precipitates in the hydrofluoric acid system. In the absence of an oxidant, the dissolution of tin is incomplete and the solubility of uranium tetrafluoride may be exceeded; if too much zirconium is dissolved, a hydrolysis-precipitation reaction may occur with the zirconium tetrafluoride. Observation of solution stability is therefore of major concern.

The technology of such waste treatment processes as calcination or precipitation does not permit any application of an advanced waste treatment process for zirconium fuels at this time. Therefore, the high volume of the aqueous waste per kilogram of uranium processed must essentially be accepted, although extensive phase studies were carried out to permit maximizing the concentration of zirconium in stored solutions, without long time precipitation.⁽⁶⁾

The development work will be reported in three phases in order to make current information generally available as quickly as possible. This document reports the basic laboratory dissolution studies and

preliminary studies of continuous dissolution techniques. The second document will present the results of more advanced continuous dissolution studies, which are still in progress. The third report will discuss the chemical flowsheet for dissolution, adjustment, solvent extraction, and waste storage. New data will be given on the continuous adjustment operation.

III. BASIC DISSOLUTION STUDIES

A. Zirconium Dissolution Rates

1. Kinetics in Hydrofluoric Acid and Zirconium Fluoride Solutions

The initial dissolution rates for Zircaloy-2 were measured in solutions containing approximately 1, 2, 5, and 10M total fluoride and various quantities of dissolved Zircaloy-2.

a. Experimental

The dissolution measurements were made at 95°C in an 800 ml Teflon beaker using 500 ml of solution. A one-liter round bottom flask coated with polyethylene and cooled with circulating water served as a condenser. Dissolution rates were determined by measuring the weight loss of Zircaloy-2 coupons which were approximately 3.5 x 1.3 x 0.5 cm. Coupons were suspended in the solution for 1 to 5 minutes depending on the dissolution rate. The solutions were sampled after each coupon dissolution, and the zirconium and acid concentrations determined. The values for fluoride were then calculated using these two values.

b. Results

Figure 1 presents the individual dissolution rates as a function of hydrofluoric acid concentrations. The hydrofluoric acid concentrations were determined by measuring the hydrogen ion concentration. In addition, the dissolution rates for Zircaloy-2 were determined in hydrofluoric acid free from zirconium, and these data are shown in Figure 1. The rate constant determined from the slope of this line is 61.2 mg cm⁻² min⁻¹ per mole HF liter⁻¹. Figure 1 shows that during the first stages of the dissolution, Zircaloy-2 dissolves at a rate corresponding to the amount of residual hydrofluoric acid present. The rate constant does not decrease until considerable zirconium has been dissolved. In solutions containing 2.3M fluoride, 65 per cent of the Zircaloy-2, which is soluble, dissolves at the dissolution rate constant for the metal in hydrofluoric acid free from zirconium. From an extrapolation of the curve for solutions containing 5.3M fluoride, it is estimated that 60 per cent of the Zircaloy-2 dissolves before the rate constant decreases. This results in a more rapid dissolution of the Zircaloy-2 than would be the case if the rate constant decreased continuously with increasing zirconium concentration as was expected.

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Fig. 1 Dissolution Rate of Zircaloy-2 as a Function of Hydrofluoric Acid Concentration and as Influenced by Total Fluoride and Zirconium Content of the Solution

Using the individual curves in Figure 1, rate constants were calculated for dissolution in solutions containing various mole ratios of fluoride to zirconium. These rate constants, shown in Figure 2, can be used to calculate dissolution rates ($\text{mg cm}^{-2} \text{ min}^{-1}$) at total fluoride concentrations other than those given in Figure 1, since the total fluoride concentration and the mole ratio define the moles of hydrofluoric acid per liter in the system. Solutions with fluoride to zirconium mole ratios of 6.5 and 7.0 and fluoride concentrations of 2.3M and 5.3M respectively dissolved Zircaloy-2 at $61.2 \text{ mg cm}^{-2} \text{ min}^{-1}$ per mole HF liter^{-1} , and therefore the fluoride concentration of this intercept is above the solid line (Figure 2); probably within the area indicated by the shaded region. The mole ratio at which the initial change in rate constant occurs is lower for lower total fluoride concentrations, and therefore, the over-all rate for a dissolution using a 10M hydrofluoric acid feed will be less than 5 times the over-all rate for a dissolution using a 2M hydrofluoric acid feed.

Figure 2 also shows that the rate constant has reached a limiting value at 4.4 moles of fluoride per mole of zirconium. A white powdery coating formed on all coupons at these low dissolution rates and decreased the rate of dissolution by as much as one-half. This film was not as evident in the higher fluoride solutions, and this no doubt accounts for the slightly higher rate constant at higher fluoride concentrations. The film was readily removed by solutions containing higher mole ratios of fluoride to zirconium.

Table 1 compares dissolution rates at various total fluoride concentrations and fluoride to zirconium mole ratios. This table illustrates the effect of the change in rate constants with the total fluoride concentration.

Table 1
DISSOLUTION RATES OF ZIRCALOY-2 AT 95°C
 $\text{mg cm}^{-2} \text{ min}^{-1}$

Mole Ratio F/Zr	4.4	5.0	6.0	Pure HF
<u>Total Fluoride</u>				
2.3M	0.1	8.5	33.0	148
5.3M	1.3	12.2	39.2	324
10.3M	1.5	24.6	57.7	630

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Fig. 2 Dissolution Rate Constants of Zircaloy-2 as Functions of Total Fluoride Concentration and Fluoride-to-Zirconium Mole Ratio

2. Initiation of the Reaction at Low Temperatures and on Oxidized Surfaces

A few scoping experiments were run to determine the minimum temperature necessary to initiate and sustain the reaction between Zircaloy-2 and the reagent or dissolver product solution of the Concentrated and Dilute Flowsheets. The reagents are 10M and 4.8M hydrofluoric acid, respectively. The material balances for these dissolutions are given in Section IV-B of this document. The rate measurements were made essentially as described above in Section III-A-1. All temperatures in Table 2 were measured prior to the initiation of dissolution. In general, the temperature rose during the measurement, and therefore the values for the reaction rate in these experiments are of lesser accuracy than those reported in Section III-A-1. The Zircaloy-2 was oxidized by autoclaving in a manner which is known to produce coatings similar to those acquired in the reactor environment.

The results listed in Table 2 indicate that the dissolution of zirconium containing fuel in dissolver reagent can be initiated and sustained at 30°C or higher in either flowsheet.

B. Chemical Forms and Properties of Uranium Tetrafluoride

Because the composition of the dissolver product solution approached so closely the known solubility values for uranium tetrafluoride, a literature and laboratory study was made of the properties of the several hydrates of the tetrafluoride. It was hoped that favorable variations in the conditions of formation or the properties might be discovered which could be exploited in the chemical flowsheet. The higher hydrate, $\text{UF}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, was reported to be less dense, have a greater surface area, and be more readily oxidized. Since this hydrate is formed preferentially at lower fluoride concentrations and lower temperatures, operation with the Dilute Flowsheet at reduced dissolver temperatures was predicted as favorable for optimum uranium solubility. No gains in solubility were predicted for increased temperature of operation.

The following are general descriptions of the different hydrates of uranium tetrafluoride.

1. Anhydrous Uranium Tetrafluoride (UF_4)

The anhydrous salt is produced by hydrofluorination of uranium oxide and by other non-aqueous processes. Generally, it will not be encountered to any extent in solutions up to 10M in fluoride. Commercial anhydrous uranium tetrafluoride was used for the solubility studies reported later. Recrystallized precipitates from solutions of this salt were hydrated, usually to the $\text{UF}_4 \cdot 3\frac{1}{4}\text{H}_2\text{O}$ species. The commercial material was not hydrated by contacting with dissolver product solutions containing 10M fluoride for two days at 95°C or for 1½ weeks at 23°C. The anhydrous UF_4 is reportedly difficult to oxidize.

Table 2

DISSOLUTION OF ZIRCONIUM FUEL

<u>Fuel</u>	<u>Dissolver Solution</u>	<u>Initial Temperature (°C)</u>	<u>Approximate Dissolution Rates (mg cm⁻² min⁻¹)</u>
Unoxidized Zr-2	2M zirconium, 10M fluoride	19	barely visible reaction
Unoxidized Zr-2	2M zirconium, 10M fluoride	30	9
Unoxidized Zr-2	1.1M zirconium, 4.8M fluoride	23	0.8
Unoxidized Zr-2	1.1M zirconium, 4.8M fluoride	30	1.4
Oxidized Zr-2	2M zirconium, 10M fluoride	24	no reaction
Oxidized Zr-2	2M zirconium, 10M fluoride	30	0.1
Oxidized Zr-2	1.1M zirconium, 4.8M fluoride	23	no reaction
Oxidized Zr-2	1.1M zirconium, 4.8M fluoride	30	barely visible reaction
Oxidized Zr-2	10M hydrofluoric acid	30	200
Oxidized Zr-2	4.8M hydrofluoric acid	30	2.8
1.5% U-Zr-2	2M zirconium, 10M fluoride	19	barely visible reaction
1.5% U-Zr-2	1.1M zirconium, 4.8M fluoride	23	0.8

2. Low Hydrates of Uranium Tetrafluoride (Mostly $\text{UF}_4 \cdot 3/4\text{H}_2\text{O}$)

The species of uranium tetrafluoride which has been consistently produced by the batch dissolution of uranium-zirconium fuel could not be identified from existing ASTM data. Better crystal preparation for X-ray analysis has now permitted identification of this precipitate as mostly $\text{UF}_4 \cdot 3/4\text{H}_2\text{O}$ with small amounts of an unidentified material. A single determination on the thermogravimetric balance indicated about $3/4 \text{ H}_2\text{O}$ per UF_4 . Dawson, D'Eye, and Truswell,⁽⁸⁾ as well as Gagarinskii and Mashirev⁽⁹⁾ discuss at some length this lower hydrate which can vary from $\text{UF}_4 \cdot 2\text{H}_2\text{O}$ down to $\text{UF}_4 \cdot 0.4\text{H}_2\text{O}$ without changing the pseudo-cubic crystalline structure. Temperature of the precipitation was noted to affect the hydrate formed. In the development of a method for the electrochemical preparation of uranium tetrafluoride,^(10,11) either the $3/4\text{H}_2\text{O}$ or the $2\frac{1}{2}\text{H}_2\text{O}$ could be formed from solutions about 3M in fluoride and 0.5M in uranium by control of temperature. The $\text{UF}_4 \cdot 3/4\text{H}_2\text{O}$ was described as a dense fine precipitate which settles rapidly. The tap density for this material was 2.7 grams per cubic centimeter and the surface area was 2.1 square meters per gram. Microscopic examination showed the material to be small amorphous particles. They report this material as difficult to oxidize.

3. Uranium Tetrafluoride Hydrate ($\text{UF}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$)

The fully hydrated salt of uranium tetrafluoride ($\text{UF}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$) can be made by slurring UF_4 for a period ranging from a few hours to a few days in 1 to 2 per cent hydrofluoric acid according to Katz and Rabinowitch.⁽¹²⁾ The physical characteristics of this hydrate are reported^(10,11) to be considerably different from those of the lower hydrate. The precipitate is described as a voluminous, easily-filtered precipitate which will not plug filters even after several weeks of operation. The tap density is 0.5 grams per cubic centimeter, or only 20 per cent as dense as the lower hydrate. Surface area is reported as 2.9 square meters per gram. Microscopic examination showed the material to be needles about 40μ in length which often cluster in groups. This hydrate can be dehydrated to the lower hydrate in a few minutes by boiling in water. This material is easily oxidized when digested for a short time with nitric acid at boiling temperature.

4. Control of Hydrate Formation

In the current study conditions were determined for the formation of the various hydrates at the process concentrations of 5M and 10M fluoride by dissolving uranium wire at controlled temperatures. These experiments showed that the lower hydrate mixture was produced at 95°C in either the 5M or 10M hydrofluoric acid as well as at 60°C in 10M hydrofluoric acid. However, at 60°C in the 5M hydrofluoric acid, the $2\frac{1}{2}$ hydrate was the major component with some of the lower hydrate still present. At 35°C , only the $2\frac{1}{2}$ hydrate was formed in both the 5M and 10M hydrofluoric acid. Since the Dilute Flowsheet with 5M fluoride is presently being favored due to the instability of dissolver effluents

from 10M fluoride flowsheets, the control of uranium species to produce the $2\frac{1}{2}$ hydrate is practicable by control of the temperature at 60°C or lower.

C. Solubility of Uranium Tetrafluoride in Dissolver Product Solutions

A limited survey was made of the solubility of uranium tetrafluoride in zirconium tetrafluoride-hydrofluoric acid mixtures which represent the dissolver product in the dissolution of zirconium fuels. The synthetic dissolver solution for these measurements was prepared by dissolving Zircaloy-2 in 10M hydrofluoric acid without oxidant and filtering off the tin solids. The initial solid phase was anhydrous uranium tetrafluoride.

The solution and solid were placed in a polyethylene bottle, purged with nitrogen, and capped tightly to prevent oxidation of the uranium. The solutions were heated for 24 hours at 95°C to simulate dissolver product solution, then maintained at the desired temperature for another 24 hours. Aliquots of the supernatant liquid were diluted with uranium-free dissolver product solution for analysis. Analyses were made using both the standard colorimetric method for total uranium and direct spectrophotometric measurement of the uranium(IV) with standards prepared from dissolver product solution. The results of these two methods were in close agreement indicating that essentially no oxidation of the uranium had occurred.

Solubility data were obtained in solutions containing a fluoride-to-zirconium mole ratio of 5.0 at 23°, 40°, 60°, and 95°C for a 10M fluoride solution and at 23°, 60°, and 95°C for 3M, 5M, and 8M fluoride solutions. No significant difference in solubility was found over this temperature range for a given solution. The average solubility values for each solution over this temperature range are given in Figure 3 together with similar data at 25°C previously reported by Argonne National Laboratory.⁽⁷⁾ The results show that the solubility of uranium tetrafluoride increases with either decreasing fluoride to zirconium mole ratio or with increasing total fluoride and zirconium concentrations. However, solutions containing 10M fluoride and low fluoride-to-zirconium mole ratios are unstable with respect to zirconium precipitation so that the most practicable flowsheets require low fluoride to zirconium mole ratios and low fluoride concentrations for stability. This is the basis for choosing a Dilute Flowsheet using 5M hydrofluoric acid.

IV. SCOPING STUDIES WITH BENCH SCALE CONTINUOUS DISSOLVERS

Two continuous dissolution systems were utilized for scoping and confirmatory studies. The first system, which used dissolvers one-half inch in diameter, was designed for long term corrosion tests of Carpenter-20 and Monel and for confirmation of the dissolution flowsheet. Each dissolver vessel, and some of the auxiliary vessels, were sacrificed for corrosion examination at the end of the long experiments.

* NUMBERS IN ARRAY INDICATE URANIUM TETRAFLUORIDE SOLUBILITY IN GRAMS URANIUM PER LITER

CPP-S-2223

Fig. 3 Solubility of Uranium Tetrafluoride in Zirconium-Hydrofluoric Acid Solutions as a Function of Fluoride Concentration and Fluoride-to-Zirconium Mole Ratio

The second system, which had a dissolver one inch in diameter, was used for scoping experiments of relatively brief duration directed toward the exploration of the process chemistry of the dissolution. This dissolver was fabricated of Monel, which appeared to be the material of choice for the chemical environment.

A. Description of Equipment

1. One-Half-Inch-Diameter Continuous Dissolver

The test equipment, shown in Figure 4, consisted of an acid feed tank, an acid feed pump, a dissolver, a dissolver off-gas condenser, a Carpenter-20(Cb) corrosion sample pot, a Monel corrosion sample pot, an off-gas condenser for the corrosion pots, a product cooler, a product solution collection vessel, and a lime bed for neutralization of product solutions. Tygon tubing was used for all connections. The double charging valve consisted of Tygon tubing attached to the top of the dissolver, and two screw clamps to seal the tubing.

Fig. 4 Miniature Zirconium Dissolver Equipment Flow Diagram

A 20-liter polyethylene bottle was used for the feed tank, a 55-liter polyethylene bottle was used to contain the lime bed, and a 1-liter polyethylene cylinder was used for the product solution collection vessel. The three heat exchangers and five of the six dissolvers were constructed of Carpenter-20(Cb); the sixth dissolver was constructed of Monel. The Monel dissolver had a nitrogen purge inlet located $\frac{1}{2}$ inch above the product solution outlet and on the opposite side of the dissolver. Details of the dissolver and corrosion pot designs are shown in Figures 5 and 6.

One corrosion coupon, made of the same metal as the dissolver, was placed in the bottom of the dissolver. A perforated polyethylene disc, resting on a support ring two inches above the bottom of the dissolver, separated this coupon from the zirconium fuel pieces in the dissolver, thus keeping the coupon in contact with fresh acid feed. Carpenter-20(Cb) corrosion coupons were placed in the Carpenter-20(Cb) corrosion pot, and Monel corrosion coupons were placed in the Monel corrosion pot. The coupons, suspended by means of Teflon wire, were located so that one coupon was in contact with the vapor, one was located at the interface, and the third was submerged in the product solution.

CPP-S-2137

CPP-S-2138

Fig. 5 Miniature Zirconium Dissolver Details

Fig. 6 Corrosion Sample Pot Details

The system was heated by electrical heating tape wrapped around the dissolver, and by hot plates under the corrosion pots. Powerstats were placed in each heater circuit to provide some temperature control. Temperatures were recorded from thermocouples on the bottom of the dissolver, the dissolver product line, the Carpenter-20(Cb) corrosion pot, the Monel corrosion pot, and the outlet line from the product cooler.

For operation the dissolver was filled with an initial charge of fuel pieces, and the heaters were turned on about ten minutes prior to feeding solvent to the dissolver. Smooth startup of all units was achieved with this procedure. Fuel piece charging was required at intervals of 10 to 45 minutes, depending upon the flowsheet and acid feed rate. Product solution volume and specific gravity were measured every 1 to 2 hours, and samples of feed and product solution for analysis and stability observation were taken once every day. A nitrogen purge rate of 0.5 scfh was maintained when the Monel dissolver was used.

2. One-Inch-Diameter Continuous Dissolver

A photograph of the one-inch-diameter laboratory Monel dissolver and auxiliary equipment is shown in Figure 7. The general arrangement

Fig. 7 Continuous Laboratory Dissolver

is similar to that for the $\frac{1}{2}$ -inch dissolver described above with the notable exception that provision was made for in-line complexing of the dissolver product solution with aluminum nitrate.

Feed solution is pumped into the bottom of the dissolver with a Sigmamotor pump; dissolver product overflows from the dissolver 16 inches above the feed inlet, passes through a Teflon corrosion coupon holder into a Monel adjustment vessel, and leaves this vessel through a tube near the top. The dissolver contains sampling ports at different heights, as well as a sampling station on the dissolver outlet. Adjustment solution enters the adjustment vessel through a tube in the top; solution in the vessel is stirred by a mechanical stirrer and is sampled through a port in the bottom of the vessel. During dissolution nitrogen gas is fed into the dissolver through a line above the dissolver outlet. Temperature within the dissolver and adjustment vessel are measured with internal thermocouples. The dissolver is heated with heating tape wrapped around the dissolution section. Lower temperatures are obtained by inserting the dissolution section into a constant temperature water bath.

B. Primary Chemical Material Balances

The initial chemical material balances for continuous dissolution of zirconium were adapted by Parrett⁽⁶⁾ from the corresponding batch dissolution flowsheets. The latter had undergone extensive laboratory tests and were supported by extensive fundamental data from studies at Argonne National Laboratory⁽⁷⁾ and the Idaho Chemical Processing Plant.⁽¹³⁾

The material balances fell, in general, into two classes. In the Concentrated Flowsheets, full advantage could be taken of the very high zirconium concentration possible in about 10M hydrofluoric acid and the high dissolution rates characteristic of that high acidity. The Concentrated Flowsheets had the inherent disadvantage of either not dissolving the uranium from fuels containing more than about one per cent uranium or requiring a relatively powerful oxidant to facilitate the dissolution.

The Dilute Flowsheet, using about 5M hydrofluoric acid, had been shown to give homogeneous batch dissolution of the zirconium and uranium from fuels of about two per cent uranium content, and it was anticipated that a continuous version of this flowsheet concept would yield similar results. The zirconium concentration in the Dilute Flowsheet, about 1.1M was about one-half that obtained with the Concentrated Flowsheet, but it had been shown⁽⁶⁾ that similar column feed solutions and raffinates could be obtained from either concentration of dissolver product solution. The concentration of zirconium in these streams is limited by the stability of the adjusted feed.

A typical Concentrated Flowsheet tested in the experiments is shown in Table 3. A typical Dilute Flowsheet is given in Table 4. Dissolvent compositions other than those shown in Tables 3 and 4 were tested in the two dissolution systems but they merely represent a modification of these basic material balances.

C. Process Chemistry Results

The results of experimental runs in the $\frac{1}{2}$ -inch-diameter dissolver are given in Table 5; those for the 1-inch-diameter dissolver in Table 6.

Table 3

CONCENTRATED CONTINUOUS DISSOLUTION FLOWSHEET FOR ZIRCONIUM
ALLOY FUEL

	<u>Charge</u>	<u>Diss. Reagent</u>	<u>Diss. Product</u>	<u>Coarse Feed Adj.</u>	<u>IAF</u>
Flow Rate		510	510	765	1275
Liters/Hour					
U g/l	1.9 kg		3.73		1.49
Zr, $\bar{M}$	93.0 kg		2.0		0.80
Al, $\bar{M}$				0.917	0.55
Sn, $\bar{M}$	1.4 kg		0.023		0.009
H ⁺ , $\bar{M}$		10.0	1.94	0.873	1.3
F, $\bar{M}$		10.0	10.0	0.375	4.23
H ₂ O ₂ , $\bar{M}$		0.01	0.005		
NO ₃ , $\bar{M}$				3.249	1.95
B g/l		1.0	1.0		0.40

Table 4

DILUTE CONTINUOUS DISSOLUTION FLOWSHEET FOR ZIRCONIUM
ALLOY FUEL

	<u>Fuel Charge</u>	<u>Diss. Reagent</u>	<u>Diss. Product</u>	<u>Coarse Feed Adj.</u>	<u>IAF</u>
Flow Rate		927	927	348	1275
Liters/Hour					
U g/l	1.9 kg		2.05		
Zr, $\bar{M}$	93.0 kg		1.10		0.80
Al, $\bar{M}$				2.02	0.55
Sn, $\bar{M}$	1.4 kg		0.013		0.009
H ⁺ , $\bar{M}$		4.84	0.374	3.77	1.3
F, $\bar{M}$		4.81	4.81	2.667	4.23
NO ₃ , $\bar{M}$		0.027(1)	0.027	7.16	1.95
B g/l		1.0	1.0		0.4

(1) Nitric acid is used for oxidation of the tin.

Table 5

CONTINUOUS DISSOLUTION OF ZIRCONIUM FUEL
UP FLOW OPERATION OF $\frac{1}{2}$ -INCH-DIAMETER DISSOLVER
AT 90°C

Run No.	Reagent Flow ml/min	Fuel	Total Run Time Hrs.	Zr M	F M	F/Zr	U g/l	% U Fuel That Could Have Been Dissolved	Dissolver Product Stability
1. 10M HF 0.03M H ₂ O ₂	6.5	1% U-Zr-2	187	2.09	10	4.9	1.10	0.6	Stable for > 1 month
2. 10M HF 0.6M HNO ₃	6.5**	Zr-2	92	2.30	10	4.5	--	--	Some Precip- itation < 1 day
3. 10M HF 0.05M H ₂ O ₂ 0.001M CuCl ₂ 0.001M MnCl ₂	7.5	1% U-Zr-2	189	2.30	11	4.9	1.89	0.9	" "
4. 10M HF	7.5	Zr-2	189	2.31	11	4.9	--	--	" "
5. 4.8M HF 0.03M HNO ₃	7.5	Zr-2	189	1.09	5.3	4.9	--	--	Stable for > 1 month
6. 4.2M HF 0.55M Al(NO ₃) ₃	7.5	1% U-Zr-2	139	0.73*	3.6*	4.9*	0.67	1.0	Stable for > 1 month

* Because of the presence of aluminum, the dissolver effluent in this run is essentially adjusted feed; the fluoride and zirconium concentrations and the mole ratio do not have the same significance as in the other experiments.

** Feed rate increased to 16 ml/min for several hours with no detectable effect on product composition.

Table 6

CONTINUOUS DISSOLUTION OF ZIRCONIUM FUEL
UP FLOW OPERATION OF 1-INCH-DIAMETER DISSOLVER
AT 90°C
(1M HYDROFLUORIC ACID REAGENT)

Run No.	Effluent Flow Rate to Fuel Surface Area Ratio (cm/min)	Fuel	Superficial Dissolution Rate mg/(cm ²)(min)	Zr (M)	F M	F/Zr Mole Ratio	U (g/l)	% U Fuel That Could Have Been Dissolved	Dissolver Product Stability at 23°C
103	0.43	Zr-2	104	2.2	11.9	5.4	--	--	Stable for > 1 month
102	0.31	Zr-2	68	2.26	12.4	5.5	--	--	Stable for > 1 month
104	0.32	Zr-2	66	2.23	11.6	5.2	--	--	Stable for > 1 month
105	0.18	Zr-2	37	2.25	11.7	5.2	--	--	Stable for > 1 month
107	0.056	2% U-Zr-2	13	2.46	11.8	4.8	2.1	1.0	Unstable at 23°C
110	0.02	3% U-Zr-2	5.1	2.53	11.4	4.5	3.5	1.5	Unstable at 92°C
112*	0.02	3% U-Zr-2	4.4	2.38	10.9	4.6	4.4	2.0	Unstable
(4.8M HYDROFLUORIC ACID REAGENT)									
106**	0.34	Zr-2	36	1.14	5.5	4.8	--	--	Stable for > 1 month
108	0.06	3% U-Zr-2	6.9	1.24	5.5	4.4	2.4	2.2	Slight precipitate immediately
109	0.06	3% U-Zr-2	7.1	1.2	5.3	4.4	2.5	2.1	Slight precipitate immediately
111	0.03	3% U-Zr-2	4.0	1.25	5.5	4.4	2.6	2.2	Slight precipitate immediately
115***	0.03	3% U-Zr-2	3.5	1.06	5.7	5.4	1.5	1.5	Slight precipitate after 8 days

* With 0.1M CrO₃

** With 0.03M HNO₃

*** Downflow operation

Operating conditions, analytical results, and observations given in these tables, are used in the correlations presented below.

1. Variation in Effluent Zirconium Concentration with Reagent Flow

The loading curves for the continuous dissolution of zirconium in several concentrations of fluoride are shown in Figure 8. There is a measurable downward trend in the zirconium concentration with increasing effluent flow rate to fuel surface area ratio or decreasing solution contact time in the dissolver. However, especially at 5.5M total fluoride, this trend is of little process significance over the rather narrow flow rate range which may be used in plant equipment. Indeed, this lack of sensitivity to flow rate may be of considerable process advantage, since it will insure product of essentially constant composition over practical flow rate ranges.

Figure 9 illustrates the relationship between the flow rate of the dissolver reagent (hydrofluoric acid) and the dissolver production rate in terms of zirconium dissolved. Since data from both dissolvers are plotted together, it was necessary to normalize to one square inch of dissolver cross-sectional area. The ratio of the abscissa value for each data point to the ordinate value is the fluoride-to-zirconium mole ratio for the product composition. The curve deviates from a straight line by the change in stoichiometry across the range of solution flows.

Fig. 8 Continuous Dissolution of Zirconium, Effluent Composition as a Function of Solution Velocity - Upflow Dissolution at 90°C

Fig. 9 Continuous Dissolution of Zirconium, Correlation of Dissolution with Reagent Flow

A straight line through the data on the log-log plot has the equation:

$$D = 0.24R^{0.94}$$

where R is the reagent flow rate in moles of fluoride/(hr)(in²) and D is the dissolver production rate in moles of zirconium dissolved/(hr)(in²).

It should be noted that the data for two dissolvers, having different sizes and operating with diverse reagent concentrations, correlates very well; therefore, the dissolver cross-sectional area may be a useful parameter for scale-up provided the subdivision of the fuel in the reactive zone of the continuous dissolvers is comparable. Although the zirconium fuel elements are initially very massive, the base of the continuous dissolver will presumably be filled with an irregular array of small fragments under steady state operating conditions. This is exactly the condition of the partially reacted fuel pieces in the base of the $\frac{1}{2}$ -inch and 1-inch diameter dissolvers used in the tests reported here. In the case of the continuous dissolution of aluminum fuels, the cross-sectional area of the dissolver has been shown to be useful for scale-up from a dissolver which was two inches in diameter, to dissolvers five inches and 7.5 inches in diameter.(5)

2. Solution Stability with Respect to Zirconium Precipitation

All effluent solutions from the dissolution experiments using the Dilute Flowsheet were stable for at least eight days, provided the fluoride to zirconium mole ratio was 4.8, or greater. Precipitation in the samples at this fluoride concentration, but lower ratio, was very small. In 10 to 12M fluoride, a mole ratio of fluoride to zirconium of 5.0 or greater was required to insure long term stability. These observations are in agreement with the more extensive studies of the stability of this system available in the literature.(7) In general, it should not be difficult to produce dissolver effluents with adequate stability for the short period prior to complexing. Indeed, it should be possible to insure stable solution for several days in order to prevent precipitation, should the processing be inadvertently halted.

3. Behavior of Uranium

a. In Hydrofluoric Acid Without Oxidants

In early continuous dissolution studies reported, the behavior of uranium was investigated to establish correlation with the fundamental uranium solubility studies reported in Section III-C and to indicate empirically, on a small scale, exactly what fuel composition could be dissolved homogeneously by hydrofluoric acid using no oxidant.

Figure 10 shows the results of uranium analysis of the effluents from the experiments of Table 6 plotting fluoride to zirconium mole ratio vs per cent uranium in the fuel dissolved homogeneously. The uranium concentrations, in grams per liter, are indicated at each data

Fig. 10 Continuous Dissolution of Uranium-Zirconium, Uranium Solubility - Dissolution at 90°C, Analysis After Filtration at 25°C

point for direct comparison with Figure 3 of Section III-C. Good general agreement is shown between the uranium solubility in the continuous dissolver effluent and the measured solubilities. Higher uranium solubilities are obtained in higher total fluoride concentrations and at lower fluoride to zirconium mole ratios. Unfortunately, uranium solubility and solution stability are optimum at different fluoride to zirconium mole ratios and fluoride concentrations. The Dilute Flowsheet represents a reasonable compromise of these and other flowsheet factors for fuels currently being considered. Experiments, to be reported later, have shown that this value of uranium in fuel dissolved homogeneously can be increased significantly by alternate dissolver operation techniques. A survey of the schedule for availability of zirconium alloy fuels for reprocessing indicates that all such fuels which are amenable to aqueous processing can be dissolved homogeneously by

the Dilute Flowsheet. In some cases blending of related fuels of high and low uranium content may be required to obtain a uniform product of flowsheet composition.

b. In Hydrofluoric Acid with Oxidants

During the batch dissolution of uranium-zirconium alloy fuels it had been shown that a reagent containing a mild oxidizing agent and hydrofluoric acid partially oxidized the uranium and subsequently increased the over-all uranium solubility.⁽⁶⁾ In these batch studies, it was not determined conclusively that any of the oxidation took place during the zirconium dissolution period. Indeed, observation of the dissolver contents after the dissolution of essentially all of the zirconium but prior to the digestion period suggested that probably the oxidation of uranium occurred during the digestion period when there was no competing reduction reaction. Consideration of the standard potentials for the various reactions involved in the dissolution indicates that oxidation of uranium-IV to uranium-VI by chromate or peroxide should not take place until all of the metallic constituents of the system, including the tin, have dissolved. Therefore, if equilibrium

conditions prevailed in the continuous dissolver, it would be impossible to oxidize uranium to uranyl in the presence of dissolving metal, and there would be no point to testing the oxidation flowsheets. A two-vessel, two-region dissolver could be designed to bring about separation of the reaction zones, but this appears to be unacceptably complex. It is possible that the tall tube continuous dissolver could be in effect a two-zone dissolver, and the following mechanism would be responsible for any oxidation of uranium which might occur. The zirconium dissolution takes place almost exclusively in the base. If the reaction kinetics of the oxidant are not favorable for either the reaction with the dissolving metal or the hydrogen gas, the oxidant may survive this reaction zone and move toward the effluent end of the dissolver where reaction with the uranium-IV may occur. The essentially quantitative recovery of the hydrogen peroxide in the dissolver effluent, which has been experienced in the experimental work, supports the supposition that this oxidant can survive the dissolution reaction zone. Data illustrating the effect of oxidants are summarized in Table 7 from Tables 5 and 6. Comparing run 112 with runs 107 and 110 indicates that the large concentration of chromic acid does indeed produce increased uranium solubility. The modest hydrogen peroxide concentrations of runs 1 and 3 were not particularly effective. The use of aluminum nitrate in hydrofluoric acid, a slurry as dissolvent, gave quantitative dissolution of the uranium present as uranium-VI. There was appreciable corrosion of Monel.

4. Composition of Solids in the Dissolver Effluent

Table 8 gives the spectrographic analysis of the solids recovered from the dissolution system of the $\frac{1}{2}$ -inch dissolver following each of 5 prolonged runs. In runs 1, 2, 3, and 5, solids containing uranium and zirconium were recovered from the dissolver in varying quantities. The small amount of solids contained in the dissolver after run 6 were free of uranium as indicated by the analysis of the solids and by the quantitative recovery of oxidized uranium in the dissolver effluent. In the 100 series runs, using the 1-inch dissolver, tin solids were present in the dissolver effluent except for run 112. Since the fuel uranium content in general exceeded the equivalent uranium solubility in the dissolver effluent solution, uranium containing solids were also found in the dissolver. In these scoping experiments, fuel containing excess uranium was used in order to establish the upper solubility limit for the given process conditions.

V. PRELIMINARY CORROSION RESULTS

A. Preparation of Materials

The dissolver tubes, corrosion pots, and location of corrosion specimens are described in Figures 4, 5, and 6. Similarly the flowsheets and conditions of operation are summarized in Table 5 and Section IV-A.

Table 7

CONTINUOUS DISSOLUTION OF ZIRCONIUM FUELS
EFFECT OF OXIDIZING AGENTS WITH HYDROFLUORIC ACID
UPFLOW OPERATION AT 90°C

Run No.	Reagent	F/Zr mole ratio	Uranium Solubility			
			Total g/l	U-VI g/l	Equivalent to Fuel Composition of % U	Dissolved from a Fuel Containing % U
107	10M HF	4.8	2.1	--	1.0	2
110	" "	4.5	3.5	--	1.5	3
112	" " + 0.1M CrO ₃	4.6	4.4	--	2.0	3
1	" " + 0.03M H ₂ O ₂	4.9	1.1	0.46	0.6	1
3	" " + 0.05M H ₂ O ₂	4.9	1.9	1.08	0.9	1
	0.001M CuCl ₂					
	0.001M MnCl ₂					
6	4.2M HF + 0.55M Al(NO ₃) ₃	4.9*	0.67	0.64	1.0	1

* With aluminum nitrate present the F/Zr mole ratio does not have the same significant effect on uranium solubility as in the absence of aluminum nitrate.

Table 8
SOLIDS COMPOSITION
DISSOLUTION RUNS OF TABLE V

Flowsheet	Sample Description	Zr	U	Sn	Al	Cr	Cu	Fe	Mn	Ni	Si	Zn
1. 10M HF - 0.03M H ₂ O ₂	Solids in C-20 corrosion pot	40%	15%	1%	T		T	m	T	m	T	m
	Solids in Monel corrosion pot	40%	15%	1%	T		T	m	T	m	m	m
	Solids in	40%	1%	0.8%	T		-	m	T	m	T	m
	Product Solution	40%	10%	1%	T		T	m	T	m	m	m
2. 10M HF - 0.6M HNO ₃	Solids in C-20 corrosion pot when system plugged with solids	M		m	T	T	T	m	T	T	T	
	Solids in Monel corrosion pot when system plugged with solids	M		m	T	T	m	m	T	T	T	
3. 10M HF - 0.05M H ₂ O ₂ - 0.001M CuCl ₂ - 0.001M MnCl ₂	Solids in Product Solution	M		m	T	T	T	T	T	m	m	
		M		M	T	T	T	m		m	T	
		M		T			T			m	T	
		M		T			T			T		
		M		T			T				T	
		M		T	T		T	T		T		
	Solids in dissolver at shutdown	m	M		T		T	T	T		T	
	Solids in nitrogen purge inlet at shutdown	M	m	m	T		T	T	T	m	T	
5. 4.8M - 0.03M HNO ₃	Solids in product solution	M		m		m	T	T	T	m	m	
6. 4.2M HF - 0.55M Al(NO ₃) ₃	Solids in dissolver at shutdown	M		m	M	T	T	m	T	m	T	
	Solids in dissolver at shutdown which were soluble in 6N HNO ₃	M		m	M	T	T	m	T	T	m	

NOTE: - Indicates sought, but not found.
T Trace (less than 0.1 weight per cent)
m Minor (0.1 to 5 weight per cent)
M Major (greater than 5 weight per cent)

The dissolver for run 3 of Table 5 was made of as-welded Monel; Carpenter-20(Cb) was used for the other five runs. The Carpenter-20(Cb) dissolvers for run 1 and the first 25-3/4 hours of run 2 were annealed by soaking the vessels at 2050°F for 15 minutes. The Carpenter-20(Cb) dissolvers for the last 66-3/4 hours of run 2 and runs 4, 5, and 6 were annealed by soaking the vessels at 2050°F for 45 minutes.

The details of the preparation of the corrosion coupons are included in the tabulated results which follow.

B. Results of Evaluation

The detailed results of the corrosion evaluations are given in Tables 9 through 14. Each table is discussed briefly and a general conclusion is given at the end of the section.

The data in Table 9 suggest that both Monel and Carpenter-20(Cb) (with or without heat treatment) are satisfactory materials for vessels handling dissolver product solution from the 10.0M HF - 0.03M H₂O₂ flowsheet. However, contact with the dissolver feed at the inlet resulted in deep longitudinal grooves in the Carpenter-20(Cb) dissolver tube and mild general attack on a Carpenter-20(Cb) coupon in contact with the feed solution a short distance away. On the basis of this evidence and Table 11, Monel appears to be better suited as a material for the 10.0M HF - 0.03M H₂O₂ flowsheet. Carpenter-20(Cb) can be used if it is protected from fresh incoming dissolvent.

The data in Table 10 indicate that neither Monel nor Carpenter-20(Cb) is suitable for handling the 10.0M HF - 0.60M HNO₃ flowsheet, although Monel was somewhat more resistant to the dissolver product solution than was Carpenter-20(Cb). The Carpenter-20(Cb) corrosion pot suffered a nozzle failure in 68.5 hours, which was equivalent to a corrosion rate of 0.72 ipm; the dissolver tubes showed as great or a greater rate of attack. Carpenter-20(Cb) suffered catastrophic attack in the dissolver feed solution. No data were obtained with Monel in dissolver solution; however, Monel probably would not be fully satisfactory in this service.

Table 11 lists the corrosion resistance of the alloys for the 10.0M HF - 0.03M H₂O₂ flowsheet containing 0.001M CuCl₂ and 0.001M MnCl₂. Service test observations indicate that both annealed Carpenter-20(Cb) and as-welded Monel are suitable for this flowsheet over 189 hours. The Mn⁺⁺ and Cu⁺⁺ salts were added in an effort to catalyze the peroxide oxidation of uranium-IV to uranium-VI; part of the uranium remained in the plus four state in these experiments.

Table 12 suggests that both Carpenter-20(Cb) and Monel can be used in aerated 10-molar HF flowsheet service, with or without subjecting the Carpenter-20(Cb) to a heat treatment. At temperatures below 160°F, Carpenter-20(Cb) suffered only mild corrosion in the incoming dissolver feed solution. At a somewhat higher temperature (190°F), the alloy also resisted the dissolver product solution during the 189-hour exposure. At a temperature of 180 to 190°F, Monel coupons which were immersed

Table 9

CORROSION OF MONEL AND CARPENTER-20(Cb)
DURING DISSOLUTION OF ZIRCONIUM-URANIUM FUEL IN RUN NUMBER 1

0.03M H ₂ O ₂ - 10.0M HF Dissolvent - 188 hr Exposure				
<u>Alloy and Test Sample</u>	<u>Environment</u>	<u>Specimen Treatment</u>	<u>Temperature of Exposure (°F)</u>	<u>Corrosion Rate (ipm)</u>
<u>Monel</u>	<u>Diss. Product</u>	As-received, unwelded & machined		
coupons	liquid		180-200	0.0005
coupons	liquid		180-200	0.0007
coupons	vapor		180-200	0.0008
coupons	vapor		180-200	0.0011
pot	liq. - vapor		180-200	resistant
<u>Carpenter-20(Cb)</u>	<u>Diss. Product</u>			
coupons	liq. - vapor	As-welded, machined & sensitized	180-200	0.0002
coupons	liquid		180-200	0.0002
coupons	liquid	Unwelded, machined & annealed	180-200	0.0002
coupons	liquid		180-200	0.0002
coupons	vapor		180-200	0.0003
coupons	vapor	1250°F sensitized	180-200	0.0003
pot	liq. - vapor	2050°F annealed	180-200	resistant
coupons	<u>Diss. Feed</u>	Unwelded, machined & 1250°F sensitized	100-115	0.0041
<u>Dissolver Tube</u>	<u>Diss. Feed & Diss. Product</u>	15 min annealed 2050°F	100-115	Localized attack deep groves

Table 10

CORROSION OF MONEL AND CARPENTER-20(Cb)
DURING DISSOLUTION OF ZIRCONIUM ALLOY IN RUN NUMBER 2

0.60M HNO ₃ - 10.0M HF Dissolvent - 92.5 hr Exposure				
Alloy and Test Sample	Environment	Specimen Treatment	Temperature of Exposure (°F)	Corrosion Rate (ipm)
<u>Monel</u>	<u>Diss. Product</u>	[As-received, welded & machined]		
coupons	liquid		140-190	0.0158
coupons	liquid		140-190	0.0208
coupons	vapor		140-190	0.0067
coupons	vapor		140-190	0.0056
pot	liq. - vapor		140-190	resistant
<u>Carpenter-20(Cb)</u>	<u>Diss. Product</u>			
coupons	liq. - vapor	[As-welded machined & 1250°F sensitized]	140-190	0.0527
coupons	liquid		140-190	0.0835
coupons	liquid	[Unwelded machined & 2050°F annealed]	140-190	0.0727
coupons	liquid		140-190	0.0717
coupons	vapor		140-190	0.0130
coupons	vapor	1250°F sensitized	140-190	0.0130
pot	liq. - vapor	2050°F annealed	140-190	failure ^(a)
coupons	<u>Diss. Feed</u>	Unwelded, machined, & 1250°F sensitized	100-150	0.3347
Dissolver Tube	<u>Diss. Feed</u> <u>Diss. Product</u>	2050°F, 45 min annealed	100-150	1.18 ^(b)

(a) Nozzle failure 68.5 hr, 0.72 ipm; also general attack of pot.

(b) Represents complete penetration of tube in 66.8 hr for flowsheet using 0.60M HNO₃. Two other tubes suffered complete penetration in 2.5 and 23 hr, respectively, using the same flowsheet with slightly different HNO₃ concentrations.

Table 11
CORROSION OF MONEL AND CARPENTER-20(Cb)
DURING DISSOLUTION OF ZIRCONIUM-URANIUM FUEL IN RUN NUMBER 3

0.03M H_2O_2 + 10.0M HF Dissolvent Catalyzed with $CuCl_2$ and $MnCl_2$ 189 hr Exposure				
<u>Alloy and Type Sample</u>	<u>Environment</u>	<u>Specimen Treatment</u>	<u>Temperature of Exposure (°F)</u>	<u>Corrosion Rate (ipm)</u>
<u>Monel</u>	<u>Diss. Feed</u>			
coupons	liquid	As-received, unwelded & machined	110-180 usually 130-150	0.0072
dissolver tube	Diss. Feed Diss. Product	As-welded	110-180	resistant ^(a)
pot	Diss. Product liq. - vapor	As-welded	150-200 usually 170-190	resistant
<u>Carpenter-20(Cb)</u>	<u>Diss. Product</u>			
pot	liq. - vapor	2050°F annealed	150-200 usually 170-190	resistant

(a) Fuel plate support rings underwent aggressive attack. These rings were fabricated from Monel weld wire and do not have the same composition as wrought Monel (dissolver and coupons).

Table 12

CORROSION OF MONEL AND CARPENTER-20(Cb)
DURING DISSOLUTION OF ZIRCALOY-2 IN RUN NUMBER 4

Aerated 10M HF Dissolvent - 189 hr Exposure				
<u>Alloy and Type Sample</u>	<u>Environment</u>	<u>Specimen Treatment</u>	<u>Temperature of Exposure (°F)</u>	<u>Corrosion Rate (ipm)</u>
<u>Monel</u>	<u>Diss. Product</u>			
coupons	liquid	[As-received, unwelded & machined]	180-190	0.0003
coupons	liquid		180-190	0.0003
coupons	vapor		180-190	0.0079
coupons	vapor		180-190	0.0093
pot	liq. - vapor		180-190	resistant
<u>Carpenter-20(Cb)</u>	<u>Diss. Product</u>			
coupons	liq. - vapor	[As-welded machined & sensitized]	180-190	0.0007
coupons	liquid		180-190	0.0002
coupons	liquid	[Unwelded, machined & 2050°F annealed]	180-190	0.0001
coupons	liquid		180-190	0.0003
coupons	vapor		180-190	0.0006
coupons	vapor	1250°F sensitized	180-190	0.0007
pot	liq. - vapor	2050°F annealed	180-190	resistant
coupons	<u>Diss. Feed</u>	Unwelded, machined & 1250°F sensitized	90-160 usually 140-160	0.0002
dissolver tube	<u>Diss. Feed</u> <u>Diss. Product</u>	2050°F, 45 min annealed	90-160 usually 140-160	resistant

Table 13

CORROSION OF MONEL AND CARPENTER-20(Cb)
DURING DISSOLUTION OF ZIRCALOY-2 IN RUN NUMBER 5

0.03M HNO ₃ - 4.8M HF Dissolvent - 189 hr Exposure				
<u>Alloy and Type Sample</u>	<u>Environment</u>	<u>Specimen Treatment</u>	<u>Temperature of Exposure (°F)</u>	<u>Corrosion Rate (ipm)</u>
<u>Monel</u>	<u>Diss. Product</u>			
coupons	liquid	[As- received, unwelded & machined]	180-200	0.0013
coupons	liquid		180-200	0.0013
coupons	vapor		180-200	0.0053
pot	liq. - vapor		180-200	resistant
<u>Carpenter-20(Cb)</u>	<u>Diss. Product</u>			
coupons	vapor-liq.	[As-welded, machined & 1250°F sensitized]	180-200	0.0008
coupons	liquid		180-200	0.0028
coupons	liquid	[Unwelded, machined & 2050°F annealed]	180-200	0.0024
coupons	liquid		180-200	0.0025
coupons	vapor		180-200	0.0008
coupons	vapor	1250°F sensitized	180-200	0.0007
pot	liq.-vapor	2050°F annealed	180-200	resistant
dissolver tube	Diss. Feed Diss. Product	2050°F, 45 min annealed	90-130 mostly 100	resistant

Table 14

CORROSION OF MONEL AND CARPENTER-20(Cb)
DURING DISSOLUTION OF ZIRCONIUM-URANIUM FUEL IN RUN NUMBER 6

0.55M $\text{Al}(\text{NO}_3)_3$ - 4.2M HF Dissolvent - 139 hr Exposure				
<u>Alloy and Test Sample</u>	<u>Environment</u>	<u>Specimen Treatment</u>	<u>Temperature of Exposure ($^{\circ}\text{F}$)</u>	<u>Corrosion Rate (ipm)</u>
<u>Carpenter-20(Cb)</u>	<u>Diss. Feed</u>			
coupons	liquid	1250 $^{\circ}\text{F}$ sensitized	90-150 usually 110-130	0.0074
dissolver	Diss. Feed Diss. Product	2050 $^{\circ}\text{F}$, 45 min annealed	90-150 usually 110-130	weld stress cracks
pot	Diss. Feed Diss. Product	2050 $^{\circ}\text{F}$, 45 min annealed	180-200	resistant ^(a)
<u>Monel</u>	<u>Diss. Product</u>			
pot	liq. - vapor	as-welded	180-200	0.799

(a) Fuel plate support rings underwent aggressive attack. These rings were fabricated from Carpenter-20(Cb) weld wire and do not have the same composition as wrought or weld-deposited (cast) Carpenter-20(Cb).

in this product solution and the product solution vapors suffered about 0.3 mil and 10.0 mils corrosion per month, respectively.

The 4.8M HF-0.03M HNO₃ - 1.09M Zr dissolver product solution (Table 13) from the Dilute Flowsheet corrodes Carpenter-20(Cb), but is less corrosive to Monel. The vapors corrode Monel, but are less corrosive to Carpenter-20(Cb). Variations in heat treatment of Carpenter-20(Cb) failed to produce measureable differences in the corrosion rate. For limited service -- up to at least 189 hours -- either of the alloys tested appears satisfactory. Data from Table 13 generally suggest that Carpenter-20(Cb) is the preferred material. However, a reduction of the observed corrosion rate associated with the Monel in the dissolver product solution vapors might be achieved by operation under air-free vapor conditions.

Monel was unsatisfactory in the 4.2M HF - 0.55M Al(NO₃)₃ flowsheet, failing completely (Table 14). The presence of weld stress cracks in the Carpenter-20(Cb) dissolver tube indicates that this alloy also would be unsatisfactory for extended use with the aluminum nitrate-hydrofluoric acid flowsheet. Since the dissolver had been carefully annealed, the risk of using Carpenter-20(Cb) under these conditions is emphasized.

C. Conclusions of Corrosion Studies

These experiments indicated, in general, that Monel and Carpenter-20 were suitable for service in 10-molar hydrofluoric acid even under mild oxidizing conditions as with dilute hydrogen peroxide. Neither material would be suitable for long-term use with the more concentrated oxidant solutions. Monel may be preferred over Carpenter-20 because of the possibility that the latter may not be adequately annealed in the field and may fail at sensitized areas in or adjacent to welds, whereas Monel can be satisfactorily field-welded.

VI. CORRELATION OF DISSOLUTION RATE DATA

It is not always possible to determine whether a tall, column-type continuous dissolver is operating essentially as a stirred tank or in a true countercurrent manner with significant solution concentration gradients along the length of the column. If in a given dissolution system, the chemistry as well as the geometry of the dissolver can be shown to favor one of these models, then certain design and scale-up problems are greatly simplified. Most actual dissolution systems are intermediate in their characteristics. When zirconium is dissolved continuously in hydrofluoric acid, and especially at low solution velocities, an examination of the fuel residues in the dissolver following a run invariably indicated only that fuel immediately adjacent to the reagent inlet was being attacked aggressively by the solution. This suggests that the product solution concentration should be relatively insensitive to factors of contact time or solution velocity, and fuel surface area. This is illustrated by the loading curves of Figure 8.

If the attack on the fuel is limited to a relatively small area of the dissolver and fuel, as observations suggest, very little dissolution occurs during most of the superficial dissolution contact time on most of the fuel surface and then this dissolution proceeds only at a rate characteristic of the dissolver product solution. To explore this concept, the superficial dissolution rates* observed for zirconium during two series of experiments were plotted in Figure 11 as a function of the solution velocity** through the dissolver. The specific dissolution rates*** for the reagent and for the dissolver product solution at 4.5 moles of fluoride per mole of zirconium are also shown. At the lower solution velocities, the region of current process interest, the superficial dissolution rates approach the specific dissolution rates observed for dissolver effluent type solutions. These should coincide exactly at very low solution velocities just as the dissolution rate for the pure reagent should be approached at higher solution velocities. This correlation suggests that the tall column continuous dissolver for zirconium, when operated at low solution velocities, can be considered as a stirred tank with the bulk of the dissolution time being consumed and the bulk of the fuel surface area being exposed at dissolver effluent conditions. Figure 11 also may offer a convenient basis for evaluation of various other dissolution material balances for zirconium in hydrofluoric acid and dissolver operating conditions. It can also be seen that specific dissolution rate data, which can be determined very readily in the laboratory, can be extrapolated to continuous dissolver behavior.

VII. CONCLUSIONS

Kinetic studies of the reaction of Zircaloy-2 with hydrofluoric acid showed that dissolution rates satisfactory for a high capacity continuous dissolver can be obtained even with oxidized fuel surfaces. The solubility of uranium tetrafluoride was shown to be greatest at high concentrations of total fluoride and low fluoride to zirconium mole ratios. The Dilute Flowsheet, wherein the dissolver effluent has a zirconium concentration of 1.1M and total fluoride concentration of about 5M, gives satisfactory uranium solubility for a fuel containing 2 per cent uranium over-all. Continuous dissolution on this flowsheet was feasible in bench scale equipment and there were no evidences of factors which would prevent scale-up. Monel was preferred for the material of construction

* Superficial dissolution rate-weight of zirconium dissolved in a continuous dissolver per unit time and unit area of fuel.
(mg cm⁻² min⁻¹)

** Solution velocity-effluent flow rate to fuel surface area ratio.
(cm min⁻¹)

*** Specific dissolution rate - The dissolution rate as determined from the weight loss of a coupon of known area exposed for a brief period to a solution of essentially constant composition.
(mg cm⁻² min⁻¹)

Fig. 11 Continuous Dissolution of Zirconium, Correlation of Dissolution Rate Data - Upflow Operation of Continuous Dissolver at 90°C

over Carpenter-20 primarily because of the difficulty of obtaining good field annealing after welding with the latter material. Active oxidizing substances were shown to be very corrosive to Monel in the fluoride solutions and their concentration must be limited.

Further studies are required to define the behavior of uranium more closely, verify the performance of Monel as the material of construction, and secure additional data on continuous dissolver operation.

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