



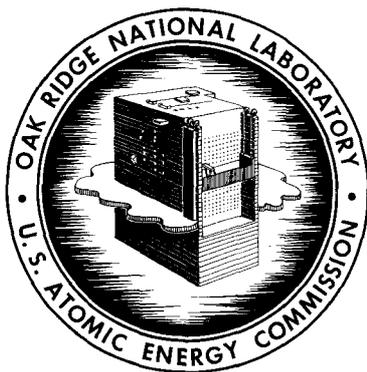
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ZIRCEX AND MODIFIED ZIRFLEX PROCESSES  
FOR DISSOLUTION OF 8% U-91% Zr-1% H  
TRIGA REACTOR FUEL

T. A. Gens



**OAK RIDGE NATIONAL LABORATORY**

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Chemical Development Section B

ZIRCEX AND MODIFIED ZIRFLEX PROCESSES FOR DISSOLUTION  
OF 8% U-91% Zr-1% H TRIGA REACTOR FUEL

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NOV 10 1961

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ABSTRACT

Processes were developed in the laboratory for recovery of uranium from spent TRIGA reactor fuel (8% U-91% Zr-1% H, clad in aluminum, graphite moderator plugs) by gas-phase hydrochlorination (Zircex process) at 300-800°C to separate  $ZrCl_4$  from the less volatile uranium chlorides and for dissolution of the fuel in 5.4 M  $NH_4F$ -0.33 M  $NH_4NO_3$ - $H_2O_2$  (modified Zirflex process). After nitric acid addition, solvent extraction feed solutions containing 0.1 and 0.0085 M uranium, for the respective processes, are obtained. To decrease corrosion during recovery of uranium by solvent extraction in stainless steel equipment, chloride is distilled from the Zircex product and aluminum nitrate is added to the modified Zirflex product. The uranium chloride product from the Zircex process may be dissolved in nitric acid or it may be fluorinated at 200°C to produce uranium hexafluoride. The aluminum cladding and graphite plugs are removed by hydrochlorination and burning, respectively, in the Zircex process and by dissolution in caustic solution and disintegration in cold fuming nitric-sulfuric acid mixtures, respectively, in the modified Zirflex process.

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## 1.0 INTRODUCTION

This report describes the laboratory chemical development of a Zircex (1-3) gas-hydrochlorination process and a modified Zirflex (4,5) dissolution in ammonium fluoride solution for removing the clad and graphite plugs and dissolving the core of TRIGA fuel, in preparation for solvent extraction of uranium. This fuel, used in TRIGA reactors built by the General Atomic Division of General Dynamics Corporation, is 8% U-91% Zr-1% H, 20% U-235 enrichment, clad in aluminum, and has graphite moderator plugs and disks of aluminum-samarium burnable poison (6). Only nonirradiated fuel samples were used. A principal objective of this work is to demonstrate the general applicability of these processes to all zirconium-uranium alloy fuels, of which the TRIGA fuel is representative. Engineering testing and development will be required to determine the ultimate feasibility of the processes, particularly for the new high-temperature techniques proposed in the Zircex process, and mechanical clad and plug removal should be investigated.

The presence of 1% hydrogen in the TRIGA fuel caused no major changes in the Zircex and modified Zirflex processes developed previously for uranium-zirconium alloys, but changes were necessary because of the thickness of the fuel elements, 1.416 in. dia (the PWR seed, an example of uranium-zirconium alloy fuel, is only 0.07 in. thick); the higher percentage of uranium, which necessitated the use of additional ammonium fluoride in the modified Zirflex process; and the presence of aluminum cladding, aluminum-samarium (burnable poison) disks, and graphite plugs. The TRIGA fuel did not react with nitric acid, and dissolution in hydrofluoric acid was not attempted because of the low solubility of uranium in the dissolver solution (7) and the need for a dissolver material other than stainless steel. Mixed hydrofluoric-nitric acid or hydrofluoric acid-hydrogen peroxide are excellent dissolvents for the TRIGA fuel but are very corrosive to all available construction materials. Data on the chemical reactions involved and problems such as corrosion rates and solution stability have been reported elsewhere for the Zircex (2,3) and modified Zirflex (4,5) processes.

The Zirflex process using ammonium fluoride solutions as a dissolvent for reactor fuel cladding was proposed at the Hanford Atomic Products Operation (8). Additional development work has also been done at ORNL (9, 10). Aqueous ammonium fluoride alone has been used as a dissolvent for uranium-zirconium alloys (4, 11), but uranium is precipitated as  $\text{NH}_4\text{UF}_5$  during dissolution. Uranium-zirconium alloy fuels are currently dissolved in hydrofluoric acid (Monel dissolver) at the Idaho Chemical Processing Plant (12).

Development work on hydrochlorination and chlorination processes for uranium-zirconium alloys in fluidized beds is being carried out at Brookhaven (13) and Argonne National Laboratories (14).

Analytical work was performed by G. Wilson, A. D. Horton, and R. L. Sherman of the Analytical Chemistry Division. Corrosion tests were planned by W. E. Clark of the Chemical Technology Division and run by L. Rice and co-workers of the Reactor Experimental Engineering Division. The aid of J. W. Ullmann of the Chemical Technology Division in collecting fuel specifications and making nuclear reaction yield calculations is gratefully acknowledged.

## 2.0 FLOWSHEETS

The flowsheets shown are based on previously reported (1-6, 15) and new laboratory data (Sect. 3.0). The scale used is the individual fuel element, but in practice many elements might be processed simultaneously. Because of the large size of the TRIGA fuel element, element-scale demonstration runs were not made in the laboratory, and engineering-scale runs are planned. The overall dimensions of the clad fuel are 1.476 in. o.d. x 28.5 in. long; the fuel core is 1.416 in. dia x 14 in. long; the two graphite plugs are each 1.4 in. dia x 4 in. long; and the aluminum cladding is 0.030 in. thick. Two aluminum-samarium disks in each fuel element are each 0.05 in. thick.

The Zircex treatment offers an advantage over the modified Zirflex in the smaller volumes of solvent extraction feed and high-level radioactive waste solutions (7.6 vs 90 liters per fuel element). A disadvantage is the greater engineering development work required because of the general lack of experience with high-temperature gas-solid reactions in radiochemical plants.

## 2.1 Zircex

The Zircex process (Fig. 1) involves three high-temperature operations—hydrochlorination of the aluminum cladding, the aluminum-samarium disks, and the core; chlorination of residual oxides and uranium chloride with carbon tetrachloride vapor; and burning of the graphite plugs and three aqueous steps—dissolution of selectively condensed uranium chlorides, chloride removal, and feed adjustment. About 22 hr per cycle is required. The last two steps are not shown in the flowsheet. The volatilized zirconium and aluminum hydrochlorination products are cooled and condensed to solids.

Hydrochlorination requires 1 hr at 300°C to remove the aluminum cladding (15) and 9 hr at a reaction temperature of 400-600°C for complete reaction of the core and the aluminum end fittings. Passivation of aluminum may be prevented by placing a small amount of ammonium chloride on the aluminum. Approximately 1.5% of the uranium and 97% of the zirconium are removed as volatile chlorides. The residue, consisting of nonvolatile oxides and uranium trichloride, is converted to volatile chlorides by a 0.5-hr treatment with carbon tetrachloride vapor in nitrogen carrier gas at 500-600°C. The uranium chloride is selectively condensed from the exit gases from both steps at 300°C in a chamber packed with glass wool or other suitable filtering material and recovered in water solution prior to chloride removal, feed adjustment, and solvent extraction. Chloride removal to 5 ppm is accomplished in 1 hr by distilling off nitric acid and chloride and replacing the distillate with fresh 13 M HNO<sub>3</sub> (3). Over 97% of the zirconium chloride, which has a vapor pressure of 0.3 atm at 300°C, and an estimated 100% of the aluminum chloride, which has a vapor pressure of 1 atm at 183°C, pass through the 300°C condenser and are condensed in a separate chamber at ambient temperature. In previous work with uranium-zirconium alloy fuel, uranium chloride losses to the zirconium chloride condensate were 0.1% or less (3).

Burning of the long graphite cylinders of 1.85 cm radius is expected to require about 10 hr at 700-800°C (16), although the burning rate is known to be highly dependent on variables such as purity and flow rate of oxygen

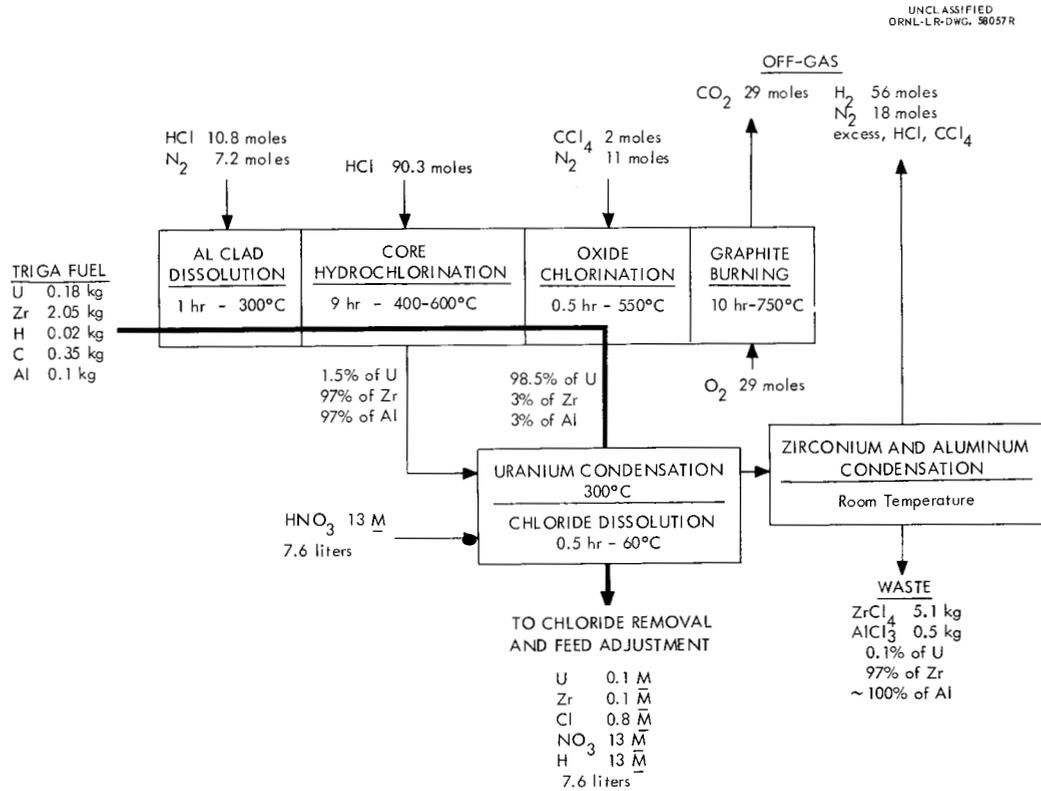


Fig. 1. Zircex process for hydrochlorination of TRIGA fuel (8% U--91% Zr--1% H).

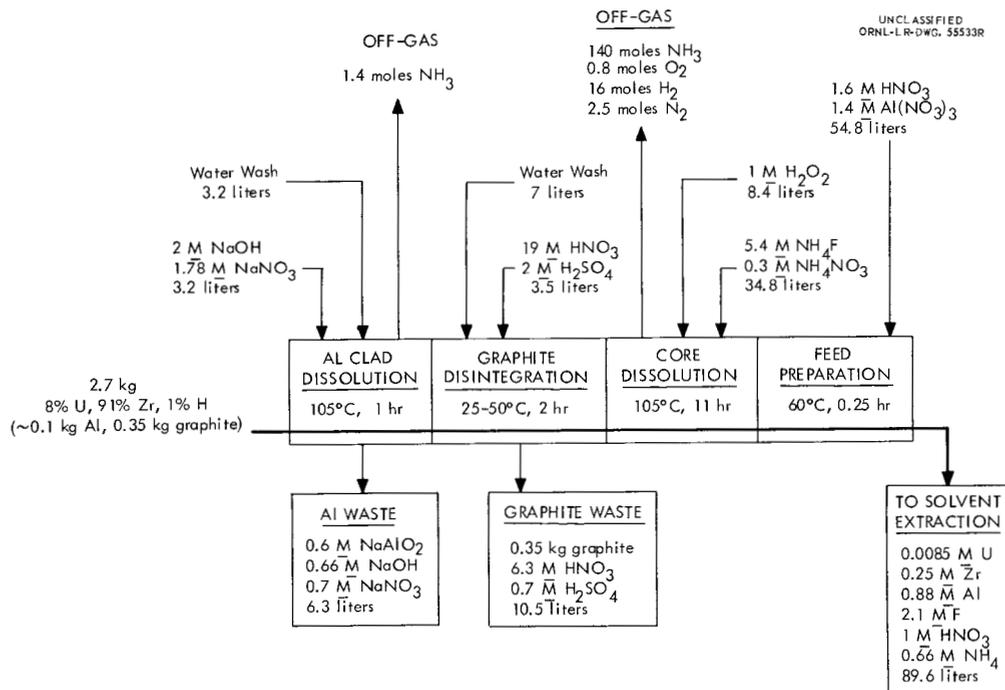


Fig. 2. Modified Zircflex process for dissolution of 8% U--91% Zr--1% H in 5.4 M NH<sub>4</sub>F--0.3 M NH<sub>4</sub>NO<sub>3</sub>--H<sub>2</sub>O<sub>2</sub>.

and purity of graphite. The product of graphite burning, if excess oxygen is used, is volatile carbon dioxide, which can probably be discharged to the atmosphere. The estimated amount of  $C^{14}$  produced at an assumed 2% burnup is  $10^{-8}\%$  of the total carbon.

The fluorination at approximately 200°C of uranium chloride in the uranium condenser to form uranium hexafluoride offers an attractive variation in the Zircox process. Experimental details have been reported elsewhere (3,17).

## 2.2 Modified Zirflex

The proposed process (Fig. 2), requiring about 14 hr per cycle, involves four main operations, all of which can probably be performed successfully in a single stainless steel vessel: aluminum cladding removal with NaOH-NaNO<sub>3</sub> (18), graphite disintegration with cold concentrated HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>, core dissolution in ammonium fluoride solution, and feed preparation by adding cold HNO<sub>3</sub>-Al(NO<sub>3</sub>)<sub>3</sub>.

Dissolution of the aluminum cladding and aluminum-samarium disks in 2 M NaOH--1.78 M NaNO<sub>3</sub> requires only 1 hr if unreacted portions of the thicker aluminum end fittings are allowed to accumulate. Such accumulation may be preferable to complete dissolution in each cycle, since on the basis of the approximately 60-mil/hr penetration rate observed in the laboratory, over 10 hr would be required to dissolve the thickest end piece (1.5 in. dia). The aluminum is not attacked during graphite disintegration or core dissolution, and is attacked only slowly (0.5 mg/cm<sup>2</sup>.min at 60°C) during the brief feed preparation step.

The technique developed for disintegration of uranium-impregnated graphite with 21 N (90%) nitric acid (19) does not work satisfactorily with the TRIGA graphite plugs which contain no uranium, although either cold or refluxing 21 N HNO<sub>3</sub> does soften and swell the graphite so that little force is needed to break up the spongy product. A mixture of cold 90% 21 N HNO<sub>3</sub>--10% 40 N H<sub>2</sub>SO<sub>4</sub> completely disintegrates the graphite plugs into fine particles in 1 hr. Careful washing is required before the graphite disintegration step to prevent a vigorous reaction between the caustic decladding

solution and the strong acid. The graphite disintegration is performed prior to core dissolution because the graphite was found to sorb an appreciable amount (up to 0.5%) of uranium if present during core dissolution and feed preparation. Very little core attack (<0.01% weight loss) occurs during the graphite disintegration. The disintegrated graphite and acid solution are flushed together to waste, along with added water. About 0.2% of the graphite dissolves in the acid solution. One hour is allowed for water addition to allow a gradual evolution of the dilution heat. Again, careful washing is required to prevent acid carryover to the core dissolution step, since acid fluoride solutions are very corrosive to most construction materials.

Core dissolution in refluxing  $5.4 \text{ M NH}_4\text{F} - 0.3 \text{ M NH}_4\text{NO}_3$  requires 11 hr. Hydrogen peroxide solution is added continuously to oxidize uranium(IV) to uranium(VI), which is more soluble under the dissolution conditions, and to lower corrosion rates (5). The concentration of the added hydrogen peroxide solution is of little importance, except that a concentration might be selected such that the volume added to the dissolvent equals the volume reduction that normally occurs during dissolution. These core dissolution conditions were chosen to minimize the amount of fluoride used, to ensure oxidation of uranium(IV) to uranium(VI) to prevent precipitation of uranium and avoid possible criticality problems, and to minimize hydrogen evolution.

In the feed preparation step, aluminum nitrate and nitric acid are added to the dissolver solution to produce a solution suitable for recovery of uranium by solvent extraction with tributyl phosphate (12). The aluminum also complexes fluoride and thus inhibits corrosion in subsequent operations.

A simplification is possible in the core dissolution step by using pure ammonium fluoride solution and permitting precipitation of ammonium uranium(IV) fluoride (4). The advantage from the 20% reduction in fluoride thus permitted might be enough to outweigh the extra precautions needed to ensure against a nuclear reaction since the U-235 enrichment in the TRIGA fuel is only 20%. If hydrogen peroxide should not be used, the ammonium nitrate would probably be omitted also since  $\text{NH}_4\text{F} - \text{NH}_4\text{NO}_3$  solutions without hydrogen peroxide are corrosive (5). Omission of ammonium nitrate would

cause the hydrogen content of the off-gas to increase from 10 to about 40% (Sect. 3.3). Dissolution in pure ammonium fluoride solution would produce a solvent extraction feed solution almost identical to that produced by the hydrofluoric acid process used at the Idaho Chemical Processing Plant (0.55 M Zr) except for the higher uranium concentration (0.019 vs 0.0018 M) (12). The aluminum waste might be eliminated by acidifying and adding it to the core dissolution during feed preparation, or the aluminum cladding could be dissolved in mercury-catalyzed nitric acid (18) to yield a solution which could be added directly to the core solution.

### 3.0 LABORATORY STUDIES

Many of the experimental data used in preparing the flowsheets in Sect. 2.0 were taken from other reports, including information on hydrochlorination of aluminum (15) and zirconium; chlorination of oxides, stability and zirconium concentration of and chloride removal from the Zircex product solution (3); and burning of graphite (16). A particularly important area where little work has been done is the distribution of fission products and plutonium ( $\text{Pu}^{238}/\text{U}^{235}$  mole ratio  $\approx 3 \times 10^{-5}$  after discharge from the reactor, assuming a 2% burnup) in the Zircex process. The laboratory work reported here was on conditions for hydrochlorination and reaction with aqueous  $\text{NH}_4\text{F}$  of the TRIGA alloy, off-gas compositions, uranium losses to the graphite, and corrosion.

#### 3.1 Reaction with Hydrogen Chloride Gas

Temperature. The lowest temperature at which appreciable reaction took place between 8% U--91% Zr--1% H and hydrogen chloride gas was about 330°C (Fig. 3a). Above furnace temperatures of 330°C, the reaction rate increased rapidly to about 20 mg/cm<sup>2</sup>·min and the temperature rose to red heat unless the hydrogen chloride was diluted with an inert gas such as nitrogen. As in previous Zircex work (2,3), some uranium chloride volatilized (Fig. 3b), particularly at the higher temperatures. The amount volatilizing was highly dependent on experimental conditions; for example, less volatilized when the hydrogen chloride was diluted with nitrogen, reflecting the lower reaction temperature.

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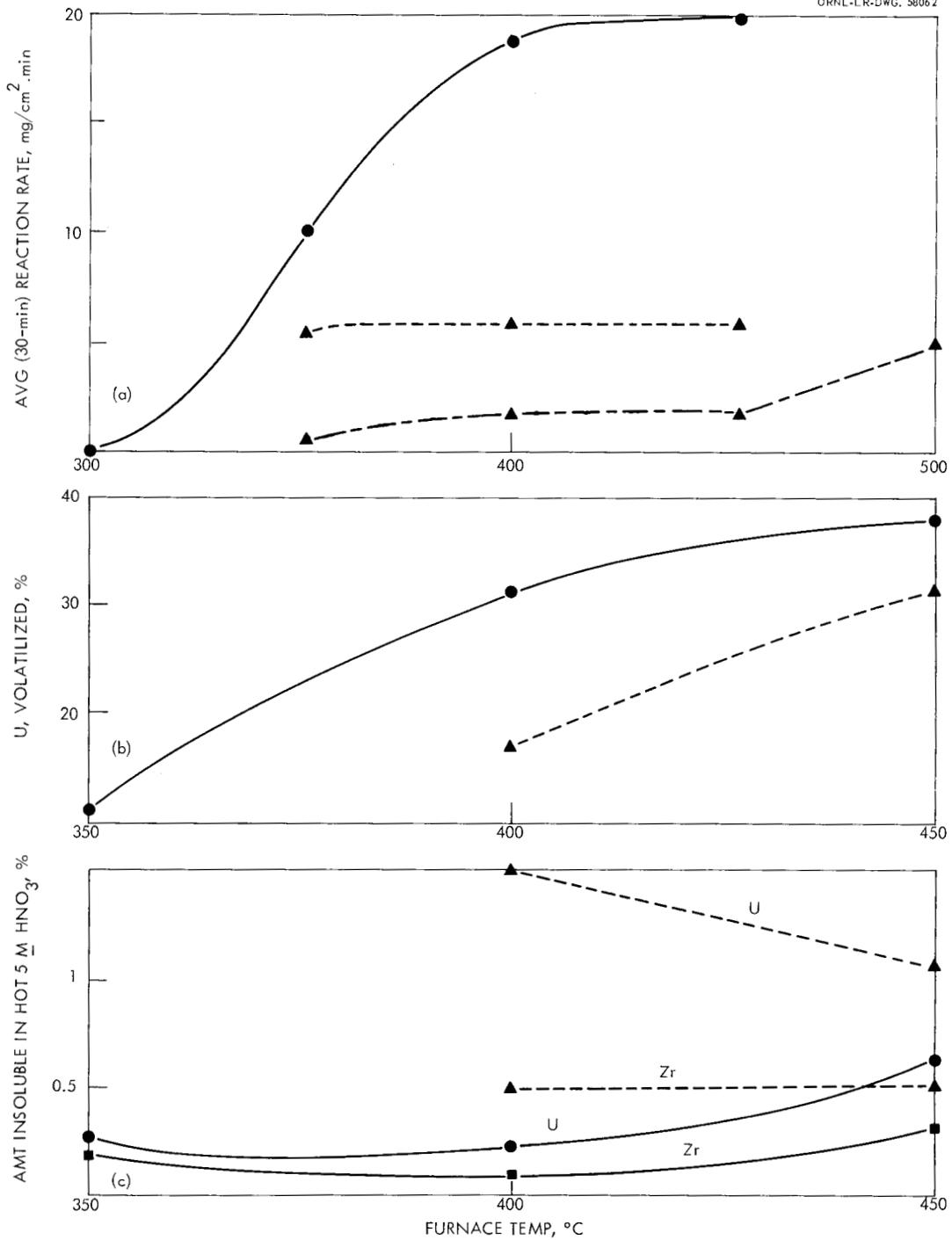


Fig. 3. Effect of furnace temperature and percentage of HCl in reagent on (a) reaction rate, (b) uranium volatilization, and (c) amount of nitric acid--insoluble uranium and zirconium produced in hydrochlorination of TRIGA fuel (8% uranium, 91% zirconium, 1% hydrogen). Fuel samples ~ 1 g, HCl at 300 ml/min; 30-min runs in 1-in.-dia tubes. pure HCl; — 50% HCl--50% N<sub>2</sub>; - - 25% HCl--75% N<sub>2</sub>.

Nitric Acid--insoluble Uranium in the Hydrochlorination Residue. Some uranium in the hydrochlorination residue was found to be in a nitric acid--insoluble form (probably  $\text{UO}_2\text{-ZrO}_2$ , formed from nonvolatile zirconium oxychloride). The amount increased or decreased roughly as the amount of nitric acid--insoluble zirconium increased or decreased (Fig. 3c). The percentage of total insoluble uranium was up to three times the percentage of total insoluble zirconium, although the weight of nitric acid--insoluble zirconium was 4-10 times the weight of nitric acid--insoluble uranium. Twenty to fifty percent of the nonvolatile zirconium was soluble in nitric acid. As previously observed in ZirceX work (2), the amount of nitric acid--insoluble material increased somewhat as the temperature increased. However, at low temperatures, the lower reaction rate with the same hydrogen chloride feed rate as was used at higher temperatures (300 ml/min) led to introduction of larger gas volumes and larger amounts of oxygen-containing impurities, which produced an opposing result of increasing the amount of nitric acid--insoluble material at low temperatures. The amount of nitric acid--insoluble material was minimum at about 400°C with pure hydrogen chloride. Oxygen-containing impurities in the nitrogen diluent gas were probably responsible for the relatively large amount of nitric acid--insoluble material found when nitrogen was mixed with the hydrogen chloride. Since the hydrochlorination residue was not completely soluble in nitric acid, an oxide chlorination was necessary (Fig. 1) to complete the conversion of the hydrochlorination residue to nitric acid--soluble chlorides (3).

### 3.2 Reaction with Ammonium Fluoride Solutions

The reaction rate of 8% U--91% Zr--1% H with refluxing 6 M  $\text{NH}_4\text{F}$  was about 20 mg/cm<sup>2</sup>·min initially (Fig. 4) and decreased as the mole ratio of F/dissolved Zr increased, becoming impractically low at less than 1 mg/cm<sup>2</sup>·min when the ratio fell below 6. The rate was highly dependent on the F/dissolved Zr mole ratio. Apparently, the 1% hydrogen content of the TRIGA fuel has little effect on the dissolution behavior in ammonium fluoride solutions since the reaction rate with a similar alloy, 7% U-93% Zr, was very similar (Fig. 4).

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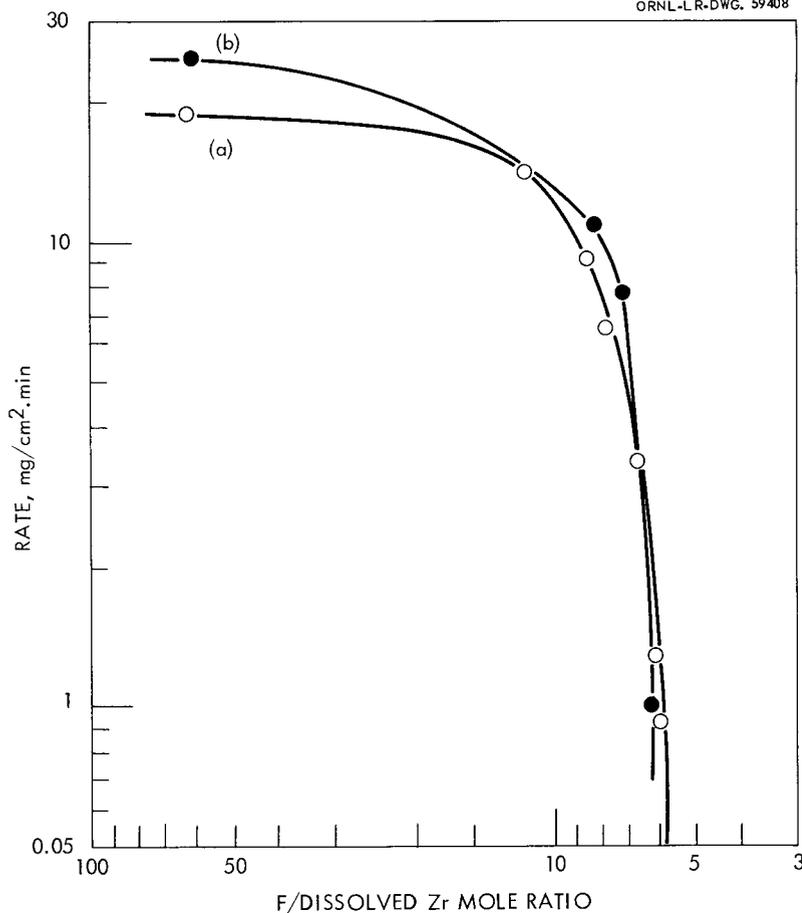


Fig. 4. Reaction rates of (a) 8% U-91% Zr-1% H and (b) 7% U-Zr with refluxing  $6 \text{ M } \text{NH}_4\text{F}$ .

Rates were determined by immersing clean, weighed specimens of alloy of known geometric surface area in  $6 \text{ M } \text{NH}_4\text{F}$  and calculating the average reaction rate from the weight loss found on removal from solution. The average amount of zirconium in solution was also calculated for each run, and the reaction rate (cm penetrated/hr) of 8% U-91% Zr-1% H in refluxing  $6 \text{ M } \text{NH}_4\text{F}$  was correlated as two linear functions of the F/dissolved Zr mole ratio:

$$R_H = 0.02 \text{ F/Zr} + 18 \quad (11 < \text{F/Zr} < \infty)$$

$$R_L = 3 \text{ F/Zr} - 15 \quad (\text{F/Zr} < 11)$$

where  $R_H$  is the rate when the mole ratio of F/dissolved Zr is greater than 11 and  $R_L$  the rate when the ratio is less than 11. The expressions fit the

experimental data very closely except in the mole ratio of F/dissolved Zr range of 11-28 where values up to 15% above experimental are given. On the basis of previous rate studies (5), the expressions are also expected to closely approximate true rates if the initial ammonium fluoride concentrations are varied over the range 4-6.5 M.

A simplification can be made in using the above expressions to yield approximate total dissolution times for arbitrarily chosen final mole ratios of fluoride to dissolved zirconium,  $(F/Zr)_F$ , by calculating the average dissolution rate over the range of the mole ratios involved. The approximated total dissolution times (Table 1, Fig. 5) arrived at in this way are probably slightly shorter than the true dissolution times. Because of the cylindrical shape of the fuel, the concentration of dissolved zirconium is a quadratic function of the distance penetrated.

Table 1. Calculated Dissolution Times of 8% U-91% Zr-1% H in 6 M  $NH_4F$  as a Function of Final Fluoride/Dissolved Zirconium Mole Ratio,  $(F/Zr)_F$

$(F/Zr)_F$	Zr, $M^a$	Pene- tration, cm, when $F/Zr=11$	Avg Rate, cm/hr		Penetration Time, hr		Total
			$\frac{7 < F/Zr}{< 11}$	$\frac{11 < F/Zr}{< \infty}$	$\frac{7 < F/Zr}{< 11}$	$\frac{11 < F/Zr}{< \infty}$	
9	$0.633x - 0.175x^2$	1.165	0.145	0.2	4.72	5.83	10.55
8.4	$0.679x - 0.188x^2$	0.97	0.135	0.2	6.51	4.85	11.36
8	$0.711x - 0.197x^2$	0.945	0.13	0.2	6.96	4.73	11.69
7	$0.802x - 0.226x^2$	0.806	0.11	0.2	9.5	4.07	13.57

<sup>a</sup>x is cm penetrated.

Effect of Ammonium Nitrate. As with U-Zr alloy (5), the addition of ammonium nitrate to oxidize the hydrogen evolved to ammonia also increased the dissolution rate of 8% U-91% Zr-1% H. The initial rate was about 50% higher,  $>30 \text{ mg/cm}^2 \cdot \text{min}$ , when the ammonium nitrate concentration was 0.3 M or higher (Fig. 6).

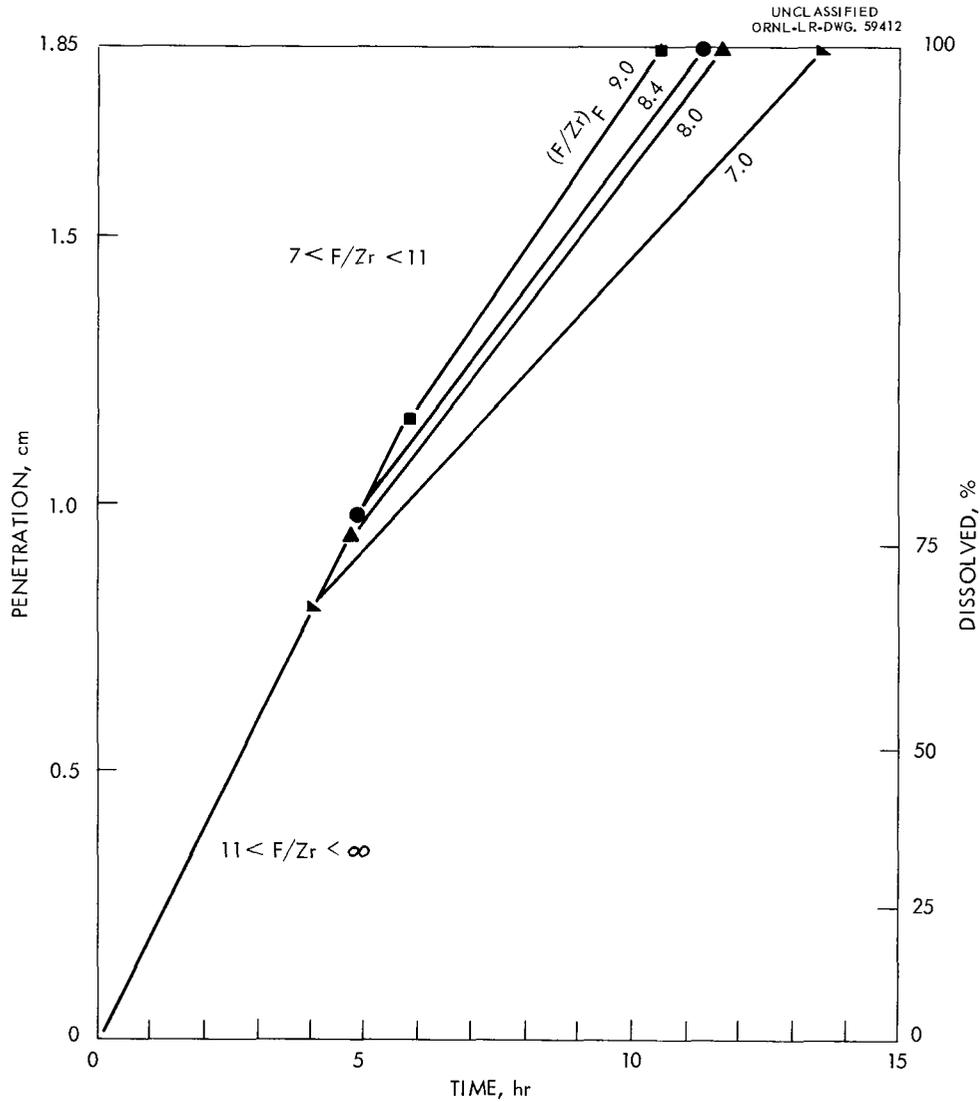


Fig. 5. Dissolution times of 8% U-91% Zr-1% H in 6 M  $\text{NH}_4\text{F}$  as a function of the final mole ratio of fluoride to dissolved zirconium,  $(\text{F}/\text{Zr})_{\text{F}}$ . Assumed average penetration rates (cm/hr):  $11 < \text{F}/\text{Zr} < \infty = 0.20$ ,  $9 < \text{F}/\text{Zr} < 11 = 0.145$ ,  $8.4 < \text{F}/\text{Zr} < 11 = 0.135$ ,  $8 < \text{F}/\text{Zr} < 11 = 0.13$ ,  $7 < \text{F}/\text{Zr} < 11 = 0.11$ .

Effect of Final Fluoride/Dissolved Zirconium Mole Ratio. Samples of up to 0.66 cm thickness dissolved completely in 4 hr in laboratory tests under the conditions given in Fig. 2 for modified Zirflex dissolution of 8% U-91% Zr-1% H (Table 2). These results agree well with the dissolution times predicted above, and larger scale tests are planned with whole fuel

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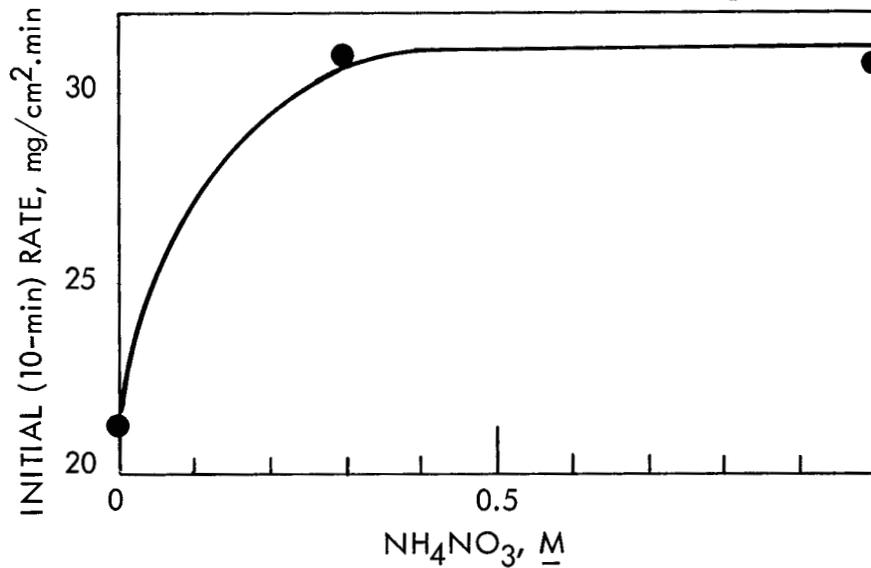


Fig. 6. Effect of ammonium nitrate on dissolution rate of 8% U—91% Zr—1% H in 5.4 M NH<sub>4</sub>F.

Table 2. Dissolution of 8% U—91% Zr—1% H Alloy (0.4-0.66 cm thick)  
in 5.4 M NH<sub>4</sub>F—NH<sub>4</sub>NO<sub>3</sub>—H<sub>2</sub>O<sub>2</sub>

Run No.	(F/Zr) <sub>F</sub>	Stoichiometric Excess, <sup>a</sup> % H <sub>2</sub> O <sub>2</sub>	NH <sub>4</sub> NO <sub>3</sub> , M	Dissolution Time, hr
1	8.4	880	0.3	3.7
2	8.3	1220	0.3	5.2 <sup>b</sup>
3	9.4	830	1.0	2.7
4	8.4	1000	0.3	5.3 <sup>b</sup>
5	8.4	1570	0.0	7.0 <sup>b</sup>

<sup>a</sup>According to the reaction  $NH_4UF_5 + 2NH_4F + H_2O_2 \longrightarrow (NH_4)_3UO_2F_5 + 2HF$ . The minimum peroxide required to maintain yellow U(VI) color was used.

<sup>b</sup>Runs 2, 4, and 5 were continued several hours after dissolution ceased, in unsuccessful attempts to dissolve a coated residue containing ~0.1% of the original sample.

elements (3.7 cm dia). In two runs made with a  $(F/Zr)_F$  of 8.4 and in one with 8.3 (Table 2), despite several hours' extra refluxing, small pieces of fuel remained undissolved. At a  $(F/Zr)_F$  of 8.4, the residue was very small, ~0.1% of the initial sample, and it dissolved during feed preparation. The undissolved pieces were coated with a green material whenever the free fluoride\* to hexavalent uranium ( $FF/U(VI)$ ) ratio fell below 70.

The minimum  $(F/Zr)_F$  of 8.4 is required for complete dissolution when U(VI) rather than U(IV) is present and corresponds to a  $FF/U(VI)$  ratio of 70 for 8% U—91% Zr—1% H. A  $FF/U(VI)$  ratio of at least 70 is also needed (5) to prevent formation of a coating which stops the dissolution of uranium-zirconium alloys containing no hydrogen in ammonium fluoride solution.

Approximately 1000% excess over the stoichiometric amount of hydrogen peroxide was needed to oxidize U(IV) to U(VI). An alternative procedure (Sect. 2.2), in which no hydrogen peroxide is added and U(IV) rather than U(VI) is produced, may be possible with TRIGA fuel, in which case the  $(F/Zr)_F$  might be as low as 6.5.

### 3.3 Off-gas

After condensation of zirconium tetrachloride, the ZirceX off-gas from hydrochlorination contained only hydrogen, unused hydrogen chloride, and small amounts of tin chloride. Acidic components, including carbon dioxide from carbon burning, may be removed by a caustic scrubber. The hydrogen may be burned or diluted by techniques proposed for radiochemical plants (20). The amount of oxygen and hydrogen evolved during modified Zirflex dissolution is of concern because of the explosive potential of these gases and the difficulty in removing them from the off-gas.

Addition of 0.3 M  $NH_4NO_3$  or more to the 5.4 M  $NH_4F$  modified Zirflex dissolvent decreased the hydrogen content of the off-gas from nearly 40% to 10% (Fig. 7). At 0.3 M  $NH_4NO_3$ , the off-gas was 0.5% oxygen, nearly 2% nitrogen, and 10% hydrogen, the remainder being ammonia. This gas should

\* Defined as  $(total \ M \ F^-) - (6Zr)$ ; assumes that 1 mole of zirconium complexes 6 moles of fluoride in the ammonium fluoride solutions.

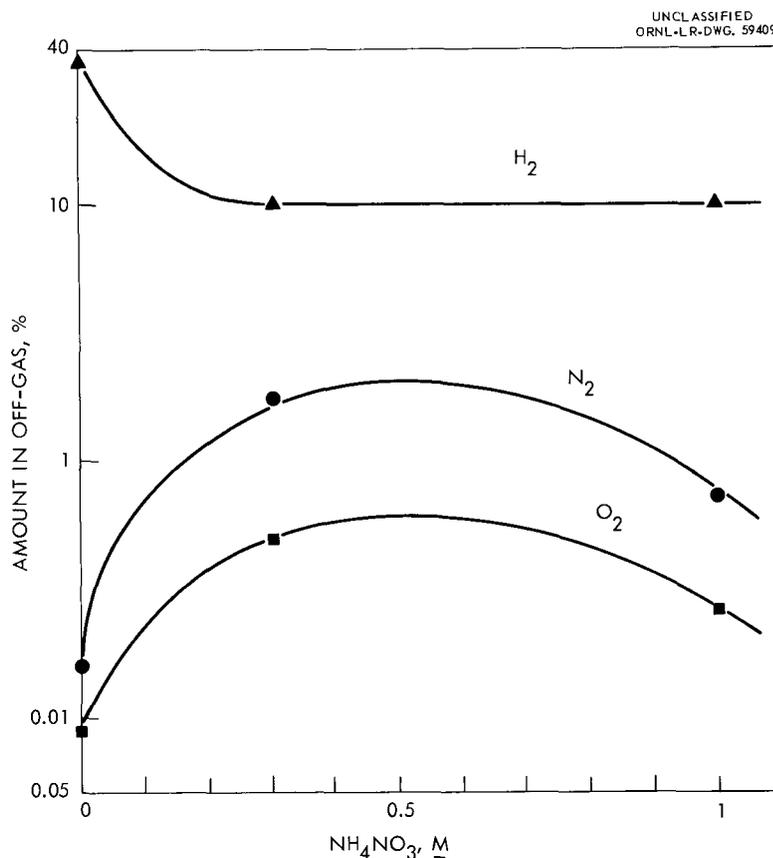


Fig. 7. Gases produced in dissolution of 8% U-91% Zr-1% H in 5.4 M  $\text{NH}_4\text{F}-\text{NH}_4\text{NO}_3-\text{H}_2\text{O}_2$ . Enough 1 M  $\text{H}_2\text{O}_2$  added continually to oxidize  $\text{U(IV)}$  to  $\text{U(VI)}$ . Remainder of gas is  $\text{NH}_3$ .

be safe to handle, since the oxygen content is low. However, if the ammonia should be removed by passing the gas through an acidic scrubbing solution, the product gas, while of small total volume, would be about 83%  $\text{H}_2$ , 13%  $\text{N}_2$ , and 4%  $\text{O}_2$ , and precautions against explosions would be needed, i.e., probably dilution with air.

The hydrogen content of this modified Zirflex off-gas agrees very well with that previously observed in dissolving 7% U-Zr alloy (5), if it is assumed that all of the 1% hydrogen content of the TRIGA fuel is evolved during dissolution. The same laboratory techniques were used in this work as described in ref. 5.

### 3.4 Uranium Absorption by Graphite

In the Zircex process (Fig. 1) absorption of uranium chloride vapor by the graphite should not lead to any loss since this uranium would be converted to nonvolatile uranium oxide during the graphite burning operation and recovered during the next chlorination. Laboratory experiments in which 1-cc cubes of TRIGA graphite were exposed to the hydrochlorination vapors for 4 hr at 400°C showed no absorption of uranium. The graphite was burned in oxygen, and the nitric acid used to wash the vessel contained no uranium.

When graphite was present during the modified Zirflex core dissolution, it absorbed uranium, and the flowsheet (Fig. 2) recommends graphite disintegration before core dissolution to avoid such loss. Samples of TRIGA graphite were exposed for 8 hr and 2 hr to refluxing final dissolver and solvent extraction feed solutions, respectively, at a reagent volume-to-graphite surface area ratio about 10 times greater than would be encountered in the actual process. The samples absorbed 0.48 and 0.35% of the total uranium, respectively.

### 3.5 Corrosion

Corrosion rates of various materials during seventy-five 11-hr hydrochlorination cycles at 600°C have been reported, with weight gained by Haynes 25, type S-816 high cobalt alloy, and Inconel at rates of 2, 39, and 67 mils/month, respectively (21). During the oxide chlorination step (Fig. 1), Nichrome V and Inconel were corroded at 1.8 and 6.5 mils/mo at 500°C and 5.5 and 18 mils/mo at 600°C, respectively. In the Zircex process, the grate needed to support the fuel should be able to withstand the 600°C temperature, while the walls, which could be cooled to facilitate heat removal by radiation during hydrochlorination, should be corrosion resistant at 350°C. Some method of supplying heat other than by heating the walls is needed during the oxide chlorination step (500-600°C) and to initiate the hydrochlorination (330°C minimum), e.g. burning of hydrogen in chlorine. The time needed for oxide chlorination can be minimized by keeping the amount of oxygen-containing impurities in the system as low as possible

during hydrochlorination. Because of the resistance of the high nickel alloys to chlorides at high temperatures, the use of nitric acid, which might corrode such alloys excessively, was avoided in the Zirnex hydrochlorinator (Fig. 1). However, an alternative procedure, in which the graphite is disintegrated in fuming  $\text{HNO}_3\text{-H}_2\text{SO}_4$  as in the modified Zirflex process (Fig. 2), might be used if a sufficiently resistant material can be found for constructing the grate, or if the grate is replaced periodically. The use of oxygen to burn carbon is not expected to produce excessive corrosion below  $800^\circ\text{C}$ . On the contrary, the presence of air has been found to greatly increase the corrosion resistance of several materials to chlorides at high temperatures (15, 22).

The results of short-term tests, which indicated low corrosion rates for several alloys in refluxing initial modified Zirflex solutions, have been reported (5). Longer term tests of 144 hr (Table 3), in which the decomposing hydrogen peroxide was continually replaced with fresh hydrogen peroxide to maintain  $0.003 \text{ M H}_2\text{O}_2$  in the refluxing  $5.4 \text{ M NH}_4\text{F}-0.3 \text{ M NH}_4\text{NO}_3$  solution, are in good agreement with the previously reported results. Hastelloy F, LCNA, and 309SNb were corroded at rates of 1-3 mils/mo in solution and at the interface and at 0.1-0.8 mil/mo in the vapor phase, the rates apparently remaining constant over the 144-hr period. Type 304L specimens were corroded at a rate of about 15 mils/mo during 24 hr in solution and at the interface, with the rate decreasing slightly with each succeeding measurement. The vapor phase corrosion rates of 304L were at least 10-fold lower than the solution and interface rates. Further tests are being made with solutions containing dissolved zirconium, which should lower the corrosion rate by complexing the fluoride. Corrosion rates of common construction materials in the cold mixed  $\text{HNO}_3\text{-H}_2\text{SO}_4$  used to disintegrate graphite (Fig. 2) have not yet been investigated.

Table 3. Corrosion of Various Alloys in Flowing 5.4 M NH<sub>4</sub>F--  
0.33 M NH<sub>4</sub>NO<sub>3</sub>--0.003 M H<sub>2</sub>O<sub>2</sub> Solutions (105°C)

Test Period, hr	Alloy	Corrosion Rate, mils/month		
		Vapor	Interface	Solution
24	304L	1.39, 0.32	14.99, 14.56	16.56, 15.73
	309SNb	0.03, 0.04	1.20, 1.48	1.65, 1.60
	Hastelloy F	0.77, 0.31	3.61, 2.25	3.35, 2.14
	LCNA <sup>a</sup>	0.17, 0.07	2.53, 2.20	2.53, 1.95
48	304L	0.72, 0.02	10.68, 9.98	9.56, 9.15
	309SNb	0.05, 0.05	1.94, 1.54	1.45, 1.42
	Hastelloy F	0.50, 0.20	2.54, 1.67	2.47, 1.71
	LCNA	0.09, 0.07	1.85, 1.63	1.89, 1.50
72	304L	0.48, 0.15	9.58, 9.10	7.74, 7.50
	309SNb	0.05, 0.05	1.48, 1.25	1.22, 1.20
	Hastelloy F	0.73, 0.22	2.22, 1.73	2.23, 1.62
	LCNA	0.10, 0.10	1.61, 1.44	1.66, 1.36
144	304L	0.26, 0.14	9.21, 9.10	7.16, 7.13
	309SNb	0.07, 0.06	1.21, 1.06	1.14, 1.13
	Hastelloy F	0.77, 0.22	2.10, 1.99	2.16, 1.76
	LCNA	0.06, 0.10	1.38, 1.28	1.43, 1.23

<sup>a</sup>A low-carbon nickel alloy having the same composition as Ni-o-nel, except for a lower carbon content (0.005%).

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