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Chemistry - Separation Processes
for Plutonium and Uranium
AEC Research and Development Report

REPROCESSING OF POWER REACTOR FUELS

TENTH QUARTERLY PROGRESS REPORT

JANUARY 1, 1960 TO APRIL 1, 1960

Compiled by

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CHEMISTRY - SEPARATION PROCESSES
FOR PLUTONIUM AND URANIUM
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ABSTRACT

Electrolytic dissolution of unirradiated Detroit-Edison core elements and of Zircaloy-2 was successfully demonstrated on a laboratory scale. Tantalum or columbium are adequate as materials of construction for the inert anode basket of an electrolytic dissolver in a field of 10^7 rep/hr. The corrosion of 304L and 309SCb in boiling HNO_3 is increased by the presence of dissolved stainless steel, which promotes intergranular attack of these metals.

Corrosion tests of both welded and wrought 309SCb indicated that a solution of 0.075M HF and 0.05 to 1M HNO_3 offers advantages over either the 0.075M HF or the 0.075M HF - 3.0M HNO_3 solutions previously proposed for the chemical dissolution of Detroit-Edison core elements. Unirradiated Zr - low U alloy was dissolved in 1M HNO_3 by intermittent addition of HF at such a rate as to obtain an average penetration rate of 4.5 mils per hour. The average composition of the off-gas was 8% H_2, 18% N_2, 50% NO, 23% N_2O, and 1% miscellaneous trace gases.

Previous reports in the series are DP-283, DP-318, DP-319, DP-338, DP-393, DP-421, DP-439, and DP-479.

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REPROCESSING OF POWER REACTOR FUELS

Tenth Quarterly Progress Report

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INTRODUCTION

Studies of the dissolution of power reactor fuels that may be processed at the Savannah River Plant were continued, the primary objective being to develop a process by which these fuels can be handled in existing stainless steel equipment. Consequently, corrosion studies of stainless steel in experimental solutions have paralleled dissolution studies of the various alloys that may be processed. Chemical dissolution of zirconium - uranium alloys in mixtures of hydrofluoric and nitric acids and electrolytic dissolution of Zircaloy-2 and uranium-molybdenum alloy clad with zirconium are discussed in this report.

SUMMARY

Unirradiated Detroit-Edison core elements (U - 10% Mo clad with 4 mils of Zr) dissolved satisfactorily in 10M HNO_3 when they were connected directly to the power source of an electrolytic cell with a cathode made of tantalum. Either a DC or AC power supply worked satisfactorily. Less than 0.005% of the total uranium was detected in the sludge formed during dissolution of the elements, after the sludge was leached for three hours in fresh, boiling 10M HNO_3. An average of 14% of the tin and zirconium in Zircaloy-2 was dissolved electrolytically; the remainder of the tin and zirconium precipitated. Tantalum and columbium were adequate as materials of construction in an electrolytic dissolver in a field of 10^7 rep/hr.

The corrosion rate of wrought 309SCb and 304L in boiling solutions that contained 0 to 30 gm/l 304 stainless steel electrolytically dissolved in 4M HNO_3 reached a peak of about 40 to 60 mils per year. The peak corrosion rate occurred in solutions that contained about 20 gm/l of dissolved stainless steel. Metallographic examination showed that intergranular attack occurred with wrought 304L, 308L welds, wrought 309SCb, and 309SCb welds. The smaller grain size of the 308L welds would account for the higher rates of corrosion observed for this metal.

Corrosion tests of both welded and wrought 309SCb stainless steel indicated that a solution of 0.075M HF and 0.05 to 1M HNO_3 offers advantages over either the 0.075M HF or the 0.075M HF - 3M HNO_3 solutions previously proposed for the dissolution of Detroit-Edison core elements. Reduced rates of corrosion of these steels were obtained by addition of 0.05 to 1M HNO_3 to 0.075M HF, and gave a more uniform type of corrosion of the wrought metal.

Unirradiated Zr - low U alloy and reactor-grade zirconium were successfully dissolved in boiling mixtures of HF - 1M HNO_3. Intermittent additions of concentrated HF were made to the solutions so as to limit

the concentration of "free" HF in solution to less than 0.1M. Average penetration rates of 4.5 mils per hour were obtained, and the maximum off-gas rates per square foot of surface were calculated to be about 0.03 SCFM. During dissolution of the Zr - low U alloy the average composition of the off-gas was 8% H_2, 18% N_2, 50% NO, 23% N_2O, and 1% miscellaneous trace gases.

DISCUSSION

ELECTROLYTIC DISSOLUTION

DETROIT-EDISON CORE ELEMENTS

Electrolytic dissolution of unirradiated Detroit-Edison core elements(1) (U - 10% Mo clad with 4 mils of Zr) was accomplished on a laboratory scale. In two tests a fuel pin (0.158 inch OD) was connected directly to the power source as the anode of an electrolytic cell. The cathode was a tantalum plate and the electrolyte was 10M HNO_3. A DC power supply was used for one run, and an AC supply for the other. Since tantalum will not pass current anodically at the voltages employed, the imposed AC potential produced a half-wave rectified current through the cell. Fewer current fluctuations were observed during electrolytic decladding with AC than with DC because the frequent current interruptions promoted uniform descaling, thus keeping the surface relatively free of ZrO_2. It was necessary to heat the solutions above 50°C before starting the current. Partway through the dissolution the voltage required to maintain 10 amperes dropped about fivefold, presumably when the cladding disappeared, and remained fairly constant until dissolution of the core was nearly complete. The voltage rose sharply near the conclusion, and the current stopped abruptly when the core was totally dissolved. The sludge was leached for 3 hours in fresh, boiling 10M HNO_3 and then dissolved in HF-HNO_3 for analysis. The loss of uranium to the residue was < 0.005%. Pertinent data are given in Table I.

TABLE I

Electrolytic Dissolution of Detroit-Edison Core Elements

			Material Distribution								
			Dissolver Solution Per Cent of			Leach Solution Per Cent of			Precipitate Per Cent of		
Run	Power Source	Average Current Utilization(a), gm/amp-hr	U	Mo	Zr	U	Mo	Zr	U	Mo	Zr
PRDC-1	DC	2.1	$\sim$100	99	13	0.005	0.8	6	< 0.005	0.2	81
PRDC-2	AC	3.3	$\sim$100	99	13	0.008	0.8	2	< 0.004	0.2	85

(a) The average of the electrolytic attack on the cladding and the combined electrolytic and chemical attack on the core

ZIRCALOY-2

Four tests have demonstrated that electrolytic dissolution of Zircaloy-2 (Zr - 1.5% Sn) is similar to that for zirconium metal. Two runs were made in 10M HNO_3, and two in 16M HNO_3. An average of 14% of the Zr dissolved, and the remainder precipitated as ZrO_2. This distribution agrees with that for zirconium. Approximately 14% of the tin also dissolved and 86% precipitated. Over-all current utilization averaged 0.71 gm/amp-hr.

ELECTROLYTIC PROPERTIES OF TANTALUM AND COLUMBIUM IN HIGH FIELDS OF RADIATION

Tantalum and columbium are the candidates for materials of construction for the anode basket in an electrolytic dissolver. Both of these metals are characterized by abnormally high overvoltages (40 v for Cb, 180 v for Ta) that make them inert during electrolytic dissolution of stainless steel or zirconium in a cell for which the impressed voltage will not exceed 10 v. Columbium or tantalum is thus a suitable material for the basket, which serves as both a container and electrical connector for the anode, unless the radiation field anticipated with a plant dissolver decreases the overvoltage to less than 10 v. A test was made to determine whether a high level of radiation, comparable to that which will be experienced in a full-scale plant dissolver, would lower the anodic overvoltage to a value that would render either of the metals unsuitable as a material of construction for the anode basket.

EQUIPMENT AND PROCEDURE

An electrolytic cell with both columbium and tantalum electrodes was suspended in a field of 10^7 rep/hr. The glass cell was contained in a metal can, and the electrodes were so mounted that the cell would be connected either with a Ta anode and Cb cathode, or with a Cb anode and either a Ta or Cb cathode. The electrolyte was 10M HNO_3. A maximum of 18 v was applied to the cell during the test.

RESULTS

Tantalum or columbium as materials of construction for the inert anode basket in an electrolytic dissolver are adequate in a field of 10^7 rep/hr. When a potential of 18 v was applied to the cell, a small diffusion current that decreased from about 2 ma to about 0.2 ma was observed during radiation exposure of 5×10^7 rep, even though no anodic dissolution or anodic oxygen was observed. The current then remained constant at 0.2 ma for exposures up to 10^9 rep, at which point the test was terminated. A marked increase in the current would have resulted had the overvoltages of tantalum or columbium been decreased to less than 18 v.

DISSOLUTION OF UO_2 IN HNO_3

The chemical dissolution of UO_2 in nitric acid will not limit the capacity of an electrolytic dissolver for handling elements of UO_2 clad with stainless steel or zirconium. This was demonstrated by measuring the rate of dissolution of UO_2 in boiling nitric acid of different concentrations.

Sintered UO_2 pellets, approximately 0.4 inch in diameter, were dissolved in boiling nitric acid. The decrease in diameter and the loss in weight were obtained at each concentration of acid as a function of time. At the higher concentrations of acid the pellet disintegrated during dissolution, making an accurate estimate of the rates of penetration difficult. The rates of penetration in 10 and 16M HNO_3 were calculated by measuring the time required to dissolve the pellet completely and assuming that no disintegration of the pellet occurred. All results are given in Table II.

TABLE II

Dissolution of Sintered UO_2 in HNO_3(a)

HNO_3, M	Rate of Penetration, mils/hr
4	1
7	3
10	370
16	740

(a) Temperature = 106 ±4°C

CORROSION OF 304L AND 309SCb IN SS-HNO_3

EQUIPMENT AND PROCEDURE

The equipment and general procedure for corrosion tests were described previously(2). Test coupons were examined metallographically after exposure to experimental solutions.

Coupons of wrought 309SCb, 309SCb metal arc welded with 309SCb, wrought 304L, and 304L Heliarc welded with 308L were tested for corrosion in boiling dissolver solutions. The solutions were prepared by anodic dissolution of 304 stainless steel at a current density of 0.5 amp/cm^2 in 4 to 8M HNO_3 at room temperature. The effect of dissolution of about 300 gm/l U in solutions prepared by anodic dissolution of 30 gm/l 304 stainless steel in 4 and 8M HNO_3 was also investigated.

RESULTS

The corrosion rate of wrought 309SCb and 304L in boiling solutions containing 0 to 30 gm/l 304 stainless steel electrolytically dissolved in 4M HNO_3 reaches a peak of about 40 to 60 mils per year. The peak corrosion rate occurs in solutions with about 20 gm/l of stainless steel, as shown in Figure 1. There is no marked effect of nitric acid from 2 to 4M in the final solution containing 30 gm/l stainless steel and 0 to 1.25M uranium.

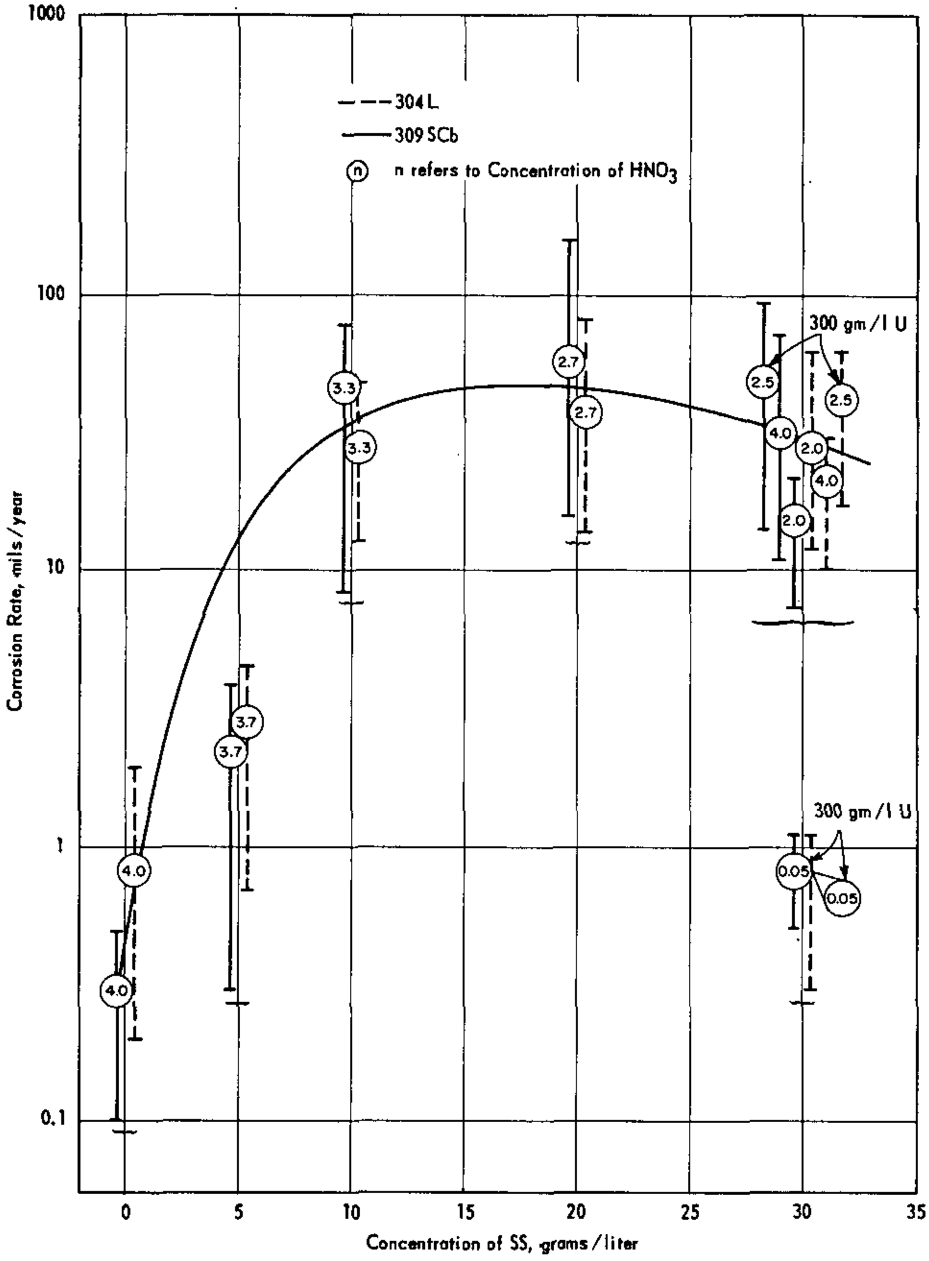

FIG. 1 CORROSION OF 304L AND 309 SCb IN SS-HNO_3 AT THE BOILING POINT

Metallographic examination of the test coupons after exposure to the electrolytic dissolver solutions showed that intergranular attack occurred with wrought 304L, 308L welds, wrought 309SCb, and 309SCb welds. The smaller grain size of 308L welds would account for the higher rates of corrosion observed for this metal in some of the tests (see Appendix).

CORROSION OF 309SCb IN $HF \cdot HNO_3$

Corrosion tests of both welded and wrought 309SCb stainless steel indicated that a solution of 0.075M HF and 1M HNO_3 offers advantages over either the 0.075M HF or the 0.075M HF - 3M HNO_3 solutions previously proposed for the dissolution of Detroit-Edison core elements (1,2,3,4) (Figure 2). Addition of from 0.05 to 1.0M HNO_3 reduced the rates of corrosion of the metal arc welds of 309SCb and the wrought metal in 0.075M HF solutions, and gave a more uniform type of corrosion of the wrought metal. A low concentration of HNO_3 in HF is also useful for the complete dissolution of fuel elements that contain mostly zirconium and small percentages of uranium, tin, and boron; it is also useful in suppressing hydrogen evolution when zirconium is dissolved in HF.

FLUORIDE VOLATILITY IN $Al(NO_3)_3 \text{-} HF \cdot HNO_3$

EQUIPMENT AND PROCEDURE

Various mixtures of HF, HNO_3, and $Al(NO_3)_3$ were distilled in a "Teflon"-lined spoolpiece, about 2 inches in diameter and 2 feet high. A condenser, made of polyethylene and containing shredded "Teflon" in the riser to prevent entrainment, was attached. About 50 ml was distilled from 500 ml of solution for each run. Total fluoride in the distillate was determined by titrating with $Th(NO_3)_4$ and using alizarin red indicator.

RESULTS

Aluminum nitrate added to boiling mixtures of HF-HNO_3 effectively reduces the fluoride volatility. As can be seen on Figure 3, an increase in the molar ratio of Al/F from 0 to 2 decreases the fluoride volatility markedly, whereas a further increase in the molar ratio has little effect. It is also apparent that increased concentrations of HNO_3 increase the volatility. These data should be useful in estimating the magnitude of corrosion caused by condensed vapor from solutions containing fluorides. It has already been shown that the corrosion rates of 304L and 309SCb stainless steel vary approximately linearly with the concentration of "free" HF(4).

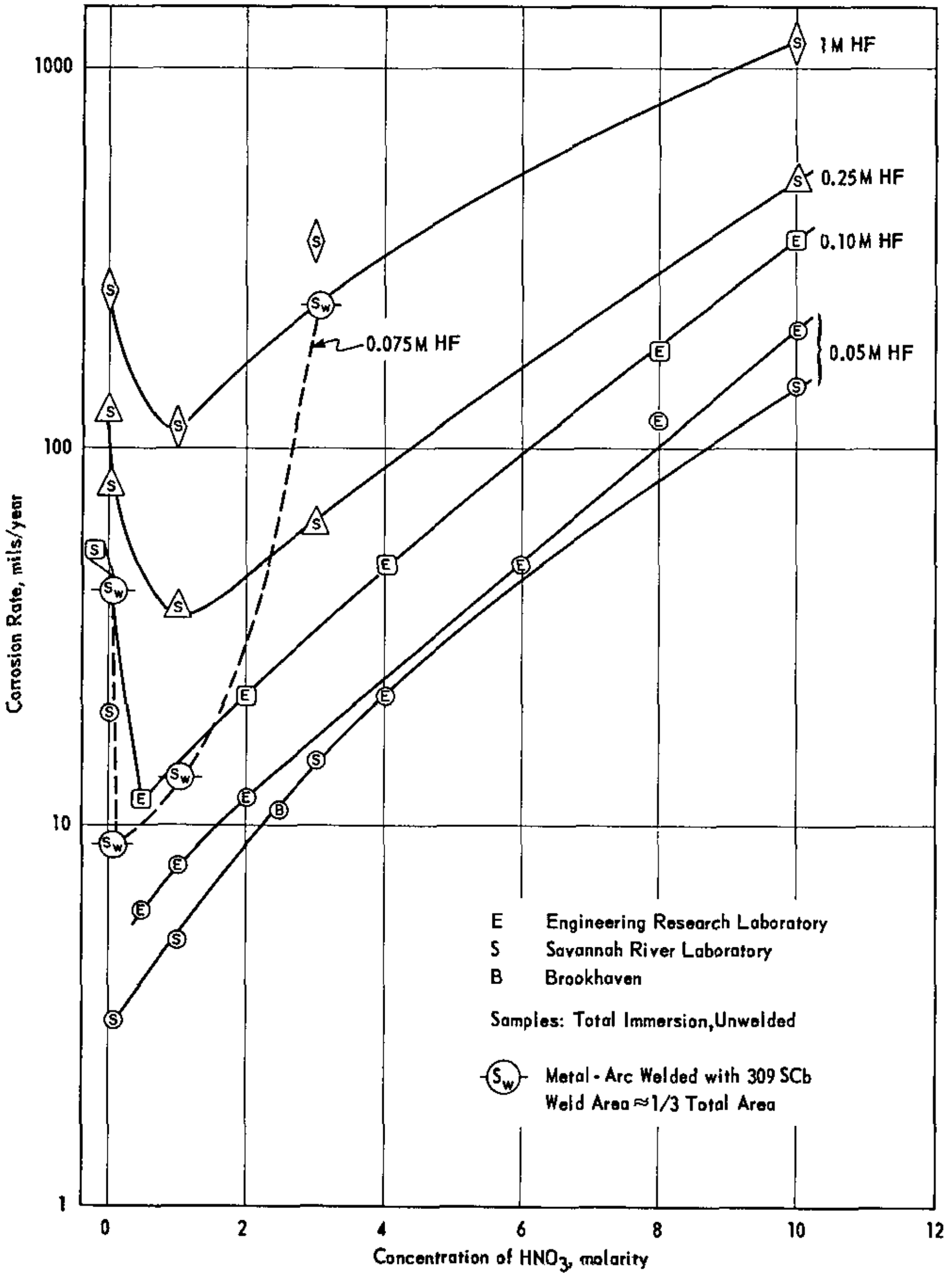

FIG. 2 CORROSION RATE OF 309 SCb IN BOILING HF-HNO$_3$

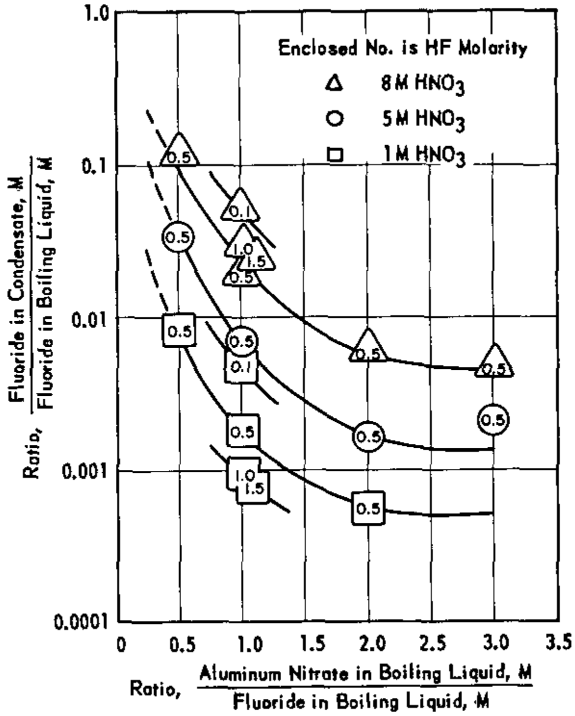

FIG. 3 VOLATILITY OF HF IN $Al(NO_3)_3$-HF-HNO_3

DISSOLUTION OF ZIRCONIUM ELEMENTS IN HF-HNO_3

EQUIPMENT AND PROCEDURE

Dissolutions of zirconium and unirradiated Zr - low U alloy were carried out using a "Teflon"-lined dissolver about 2 inches in diameter and 1 foot high with a polyethylene condenser attached. Glass equipment was used for larger-scale dissolutions.

Reactor-grade zirconium plate and Zr - low U alloy clad with Zircaloy-2 were dissolved in the "Teflon"-lined equipment in separate experiments by 200 ml of dissolvent that was initially 0.1M HF - 1M HNO_3. It was found empirically that in order to maintain a practical dissolution rate, 5 moles of HF must be added per mole of zirconium. When the amount of Zr dissolved was sufficient to reduce the concentration of HF by at least 0.05M, a corresponding amount of HF (as 48% HF) was added to the boiling solution below the liquid level. Calculations were based on dissolution rate data previously obtained in the laboratory. A conservative low penetration rate of about 4.5 mils per hour was assumed, and additions of HF were made accordingly until total dissolution, at which time a total of 5 moles of HF was added per mole of Zr charged to the dissolver. The final solution contained about 50 gm/l zirconium for all runs.

Similar runs were made with Zr - low U alloy and 1500 ml of dissolvent; laboratory glassware was used. Samples of the off-gases were taken throughout the dissolution cycle and analyzed. The final solution was analyzed for total nitrate and fluoride ions. Samples of metal-arc-welded 309SCb stainless steel were tested for corrosion in the vapor phase and in the liquid phase by making two 48-hour exposures with conventional corrosion testing equipment(2).

RESULTS

Unirradiated Zr - low U alloy and reactor-grade zirconium were successfully dissolved in separate experiments on a laboratory scale in boiling mixtures of 1M HNO_3 and HF. Complete dissolution to a final concentration of about 50 gm/l zirconium was obtained by adding concentrated HF intermittently to the boiling solution so as to limit the maximum concentration of "free" HF in the solution to less than 0.1M. An average penetration rate of 4.5 mils per hour was obtained for these runs.

During dissolution of the Zr - low U alloy the average composition of the off-gas was 8% H_2, 18% N_2, 50% NO, 23% N_2O, and 1% miscellaneous trace gases; the maximum off-gas rate per square foot of zirconium surface was calculated to be about 0.033 SCFM. This rate corresponds to about 1.5 moles of gas per mole of zirconium dissolved and a maximum penetration rate of 10 mils per hour. The off-gas rate is sufficiently low to enable reduction of the concentration of hydrogen to less than the explosives limit of 4% by air dilution in plant-scale equipment.

The final solution, which was obtained by dissolving Zr - low U alloy, was clear and stable and contained about 0.5M Zr, 0.4M NO_3, and 2.5M F. The corrosion of metal-arc-welded 309SCb was 25 to 30 mils per year in the liquid phase and 225 to 250 mils per year in the vapor phase. No preferential weld attack was observed. It is anticipated that the corrosion in the vapor phase will be reduced considerably if the off-gas is diluted with air.

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APPENDIX

Corrosion of 304L and 309SCb in SS - HNO_3

				Corrosion Rate, mils/yr(a)							
				304L				309SCb			
				Wrought		Welded(b)		Wrought		Welded(b)	
Initial HNO_3, M	Final HNO_3, M	304 SS, gm/l	U, gm/l	Average	Range	Average	Range	Average	Range	Average	Range
4	-	0		0.8	0.2-1.9	0.7	0.2-2.0	0.3	0.1-0.4	0.3	0.1-0.5
4	-	5		2.8	0.7-4.4	2.7	0.5-3.9	2.2	0.3-3.8	2.1	0-0.3
4	-	10		27	13-48	48	12-77	46	8.6-78	34	9.4-52
4	-	20		37	14-81	55	16-143	58	16-155	66	16-118
4	2.0	30		28	12-62	46	11-170	15	7.4-22	14	7.1-22
4	0.05	30	293	0.8	0.3-1.1	0.8	0.6-1.2	0.8	0.5-1.1	1.0	0.7-1.4
6	4.0	30		21	10-30	-	-	31	11-71	36	3-68
8	2.5	30	293	41	17-62	-	-	47	14-92	31	18-44

(a) In solutions at the boiling point

(b) Welded area constitutes about one-third of total area of coupon.