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DISSOLUTION OF ZIRCONIUM ALLOY FUELS IN 309 SCb STAINLESS STEEL VESSELS

Savannah River Laboratory

Aiken, South Carolina

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DISSOLUTION OF ZIRCONIUM ALLOY FUELS IN 309SCb STAINLESS STEEL VESSELS

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ABSTRACT

Tests were made to define the conditions for dissolving zirconium and zirconium-uranium alloys in 309SCb stainless steel vessels without excessively corroding the vessels. The optimum dissolvent found was an agitated solution of 1M HNO_3 at 70°C with a small stream of concentrated hydrofluoric acid injected continuously near the agitator. Under these conditions, ten tons of zirconium alloy can be dissolved in successive charges over a period of two to three weeks with less than one mil of vessel corrosion.

CONTENTS

LIST OF FIGURES

DISSOLUTION OF ZIRCONIUM ALLOY FUELS IN 309SCb STAINLESS STEEL VESSELS

INTRODUCTION

The object of this work was to define a dissolution process for zirconium alloy fuels, particularly those fuels with low uranium content. The defined process should be suitable for use in 309SCb dissolvers at Savannah River.

Zirconium-uranium alloy fuels are readily dissolved by boiling hydrofluoric acid in "Monel"* equipment(1) or by mixtures of hydrofluoric and nitric acids in a vessel resistant to this mixture. The addition of nitric acid suppresses the evolution of hydrogen, minimizes precipitation of UF_4 by oxidizing uranium to the soluble uranyl form, and dissolves the tin in Zircaloy when the latter is used as cladding(2). Although "Monel" is not a satisfactory material for containing a mixture that includes nitric acid, a program of corrosion testing(3) showed that under certain conditions the 309SCb stainless steel used in the Savannah River dissolvers is moderately resistant to attack by HF-HNO_3 dissolvent.

The aim of the current study was to find whether the conditions of solution composition and temperature that result in low corrosion of the dissolver also result in acceptable rates of dissolution of zirconium-uranium alloys.

SUMMARY

Existing data were supplemented by additional studies to allow comparison of the dissolving rates of zirconium alloys and the corrosion rate of 309SCb stainless steel over a wide range of temperatures and solution compositions. The nitric acid needed for complete dissolution of Zircaloy-2 and zirconium-uranium alloy had previously been shown to have a suppressive effect on corrosion, as long as the nitric acid concentration did not exceed 1.0M. The rates of both dissolution and corrosion were found to vary in proportion to the concentration of uncomplexed hydrogen fluoride, so that the ratio of rates was constant at a given temperature and nitric acid concentration. The data also showed that a decrease in temperature caused a greater fall in corrosion rate than in dissolution rate, and that this improvement in the dissolution-to-corrosion ratio could be retained even though the hydrogen fluoride concentration was increased to return the dissolution rate to a practical value.

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*Trademark of International Nickel Co.

The preceding observations were combined in a procedure tested at the Savannah River semiworks. A small stream of concentrated hydrogen fluoride was added continuously to a dissolver containing Zircaloy-2 plates and 1M HNO_3 at 70°C. The ratio of penetration of Zircaloy-2 to penetration of stainless steel was 5000 to 1, a value that will allow the dissolution, in successive batches, of ten tons of zirconium alloy while only one mil of the 309SCb welds is corroded from a plant dissolver. The successive dissolutions will require two to three weeks to complete.

DISCUSSION

DISSOLUTION STUDIES

Equipment and Procedure

Dissolution rates of unirradiated reactor-grade zirconium and Zircaloy-2 in HF-HNO_3 solutions were measured at the boiling point and below the boiling point. Below-boiling tests were made in a 2-liter dissolver made of polyethylene; the dissolver contained a 4-bladed paddle, 2 inches long and 1/2 inch high, made of Saran. The dissolver assembly was kept in a constant temperature bath and normally contained 1.5 liters of test solution. Measurements at the boiling point were made in a "Teflon"-lined* vessel, 1-3/4 inches in diameter and 12 inches high, which was fitted with a reflux condenser made of polyethylene; the vessel was normally filled with 400 cc of solution.

Metal samples were suspended on a polyethylene or "Teflon" holder positioned approximately half an inch from the top of the paddle blades for dissolutions at 35°C and 60°C. Mechanical agitation was not used for dissolution at boiling temperatures. The samples were periodically removed from solution, rinsed, dried, weighed, and measured.

Samples tested in solutions containing less than 0.2M HF were pretreated in HF-HNO_3 mixtures to avoid major variations in surface roughness during initial dissolving. Good reproducibility was obtained in this manner. This procedure was not necessary at higher hydrofluoric acid concentrations, since a surface of constant roughness was generated rapidly. Most of the samples were cut from flat plate that was polished to a 320-grit finish.

Results

Effect of Agitation. The dissolution rate of zirconium below boiling temperatures was affected appreciably by agitation. With low concentrations of hydrofluoric acid the relative change in rate was much greater than with high con-

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*"Teflon" is a trademark of E. I. du Pont de Nemours & Co. for fluorocarbon resins.

centrations, as shown in Figure 1. The difference is attributed to the high off-gas rate and consequent high degree of agitation at the metal surface when zirconium is dissolved in strong solutions of hydrofluoric acid. Paddle tip velocities greater than 10 ft/sec had little additional effect on the rate, and all subsequent measurements below the boiling point were made at this tip velocity.

Effect of Acid Concentration and Temperature. No differences could be found in the dissolution rates of reactor-grade zirconium and Zircaloy-2 in boiling nitric acid containing

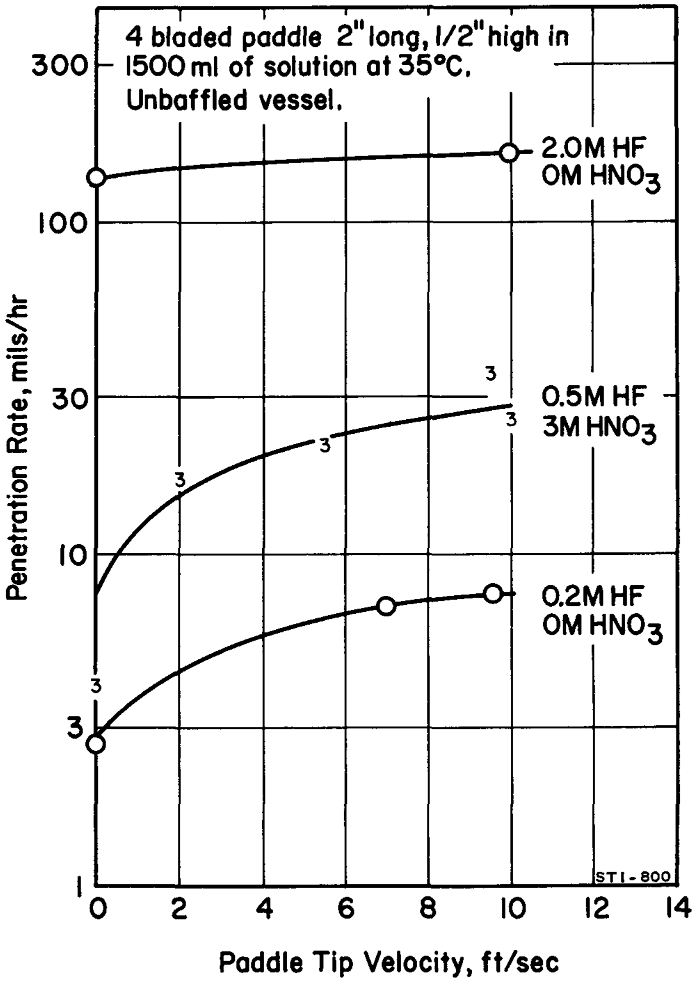

FIG. 1 EFFECT OF AGITATION INTENSITY ON DISSOLUTION RATE OF ZIRCONIUM IN HF

hydrofluoric acid; the two forms of zirconium are treated as one in the following discussion.

At the boiling point, the nitric acid concentration had only a slight effect on the dissolution rate (Figure 2). At temperatures below boiling, $3M$ HNO_3 increased the dissolution rate about a factor of two at $0.07M$ HF, but had no effect at $1.0M$ HF. Concentrations of nitric acid in excess of about $3M$ had little additional effect on the dissolution rate of zirconium in dilute hydrofluoric acid at 35°C, as shown in

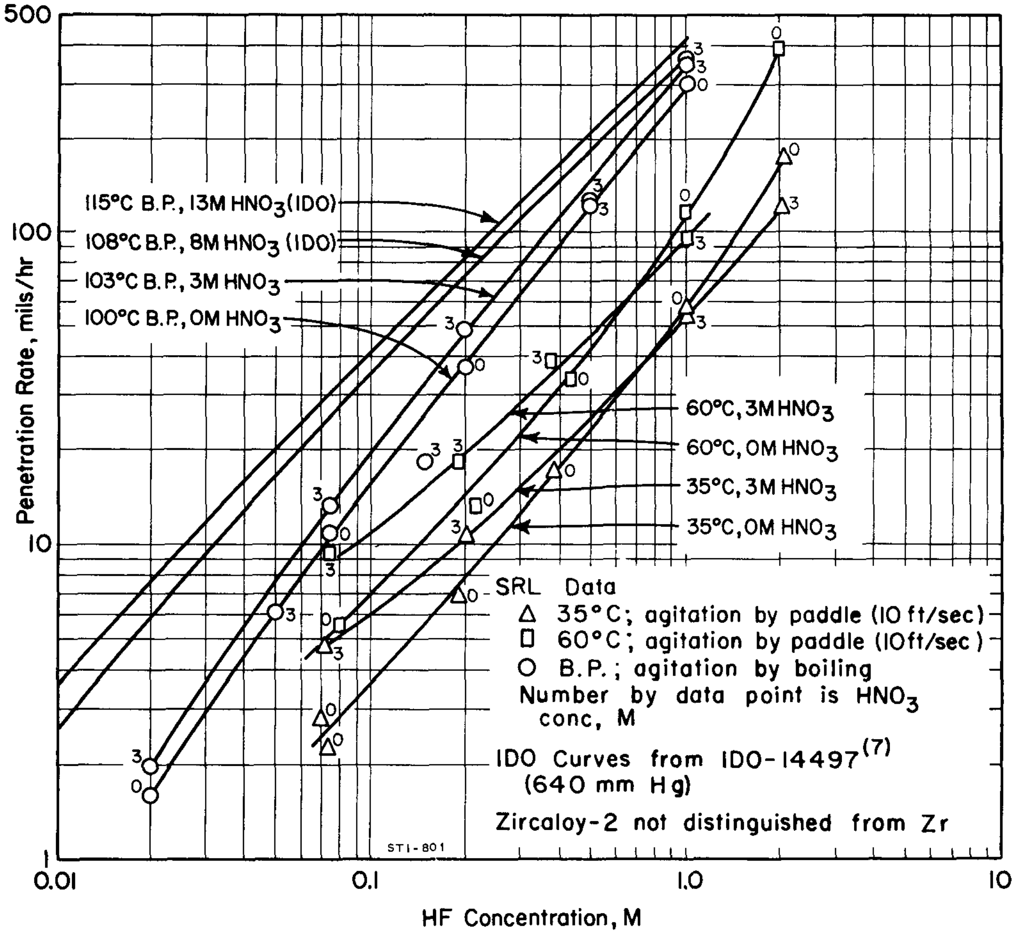

FIG. 2 DISSOLUTION RATES OF ZIRCONIUM AND ZIRCALOY-2 IN HF-HNO_3: HF CONCENTRATION AS CONTINUOUS VARIABLE

Figure 3. The samples had a dark finish when pickled in dilute hydrofluoric acid without nitric acid, but the surface acquired a luster when nitric acid was present. When the samples were viewed under a microscope, the dark surface appeared to consist of finely divided particles of metal and therefore to have a higher true surface area than that on the samples treated with mixed acid.

The effect of temperature on the dissolution rate is shown in Figure 4; an activation energy of 5.3 ±0.6 kcal/

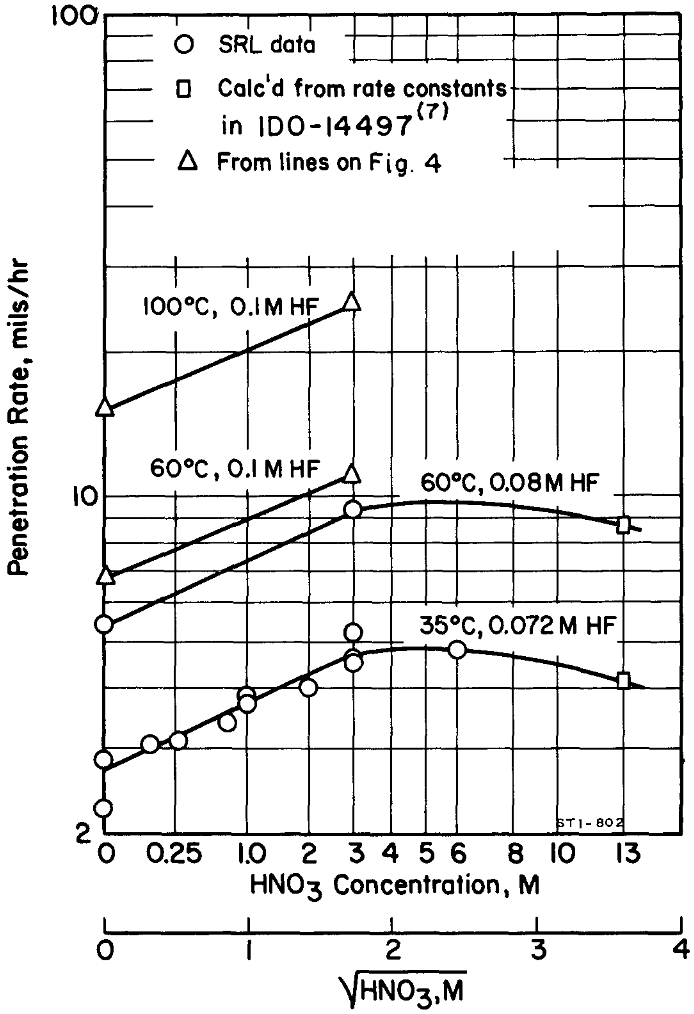

FIG. 3 DISSOLUTION RATES OF ZIRCONIUM AND ZIRCALOY-2 IN HF-HNO_3: HNO_3 CONCENTRATION AS CONTINUOUS VARIABLE

(g mol) was calculated from the slope of the lines shown. The activation energies were the same for systems with and without nitric acid.

The dissolution rate of unirradiated Zr — 9.5% U alloy in boiling solutions of hydrofluoric acid in the absence of nitric acid was about 65% of that for reactor-grade zirconium. The data are not shown.

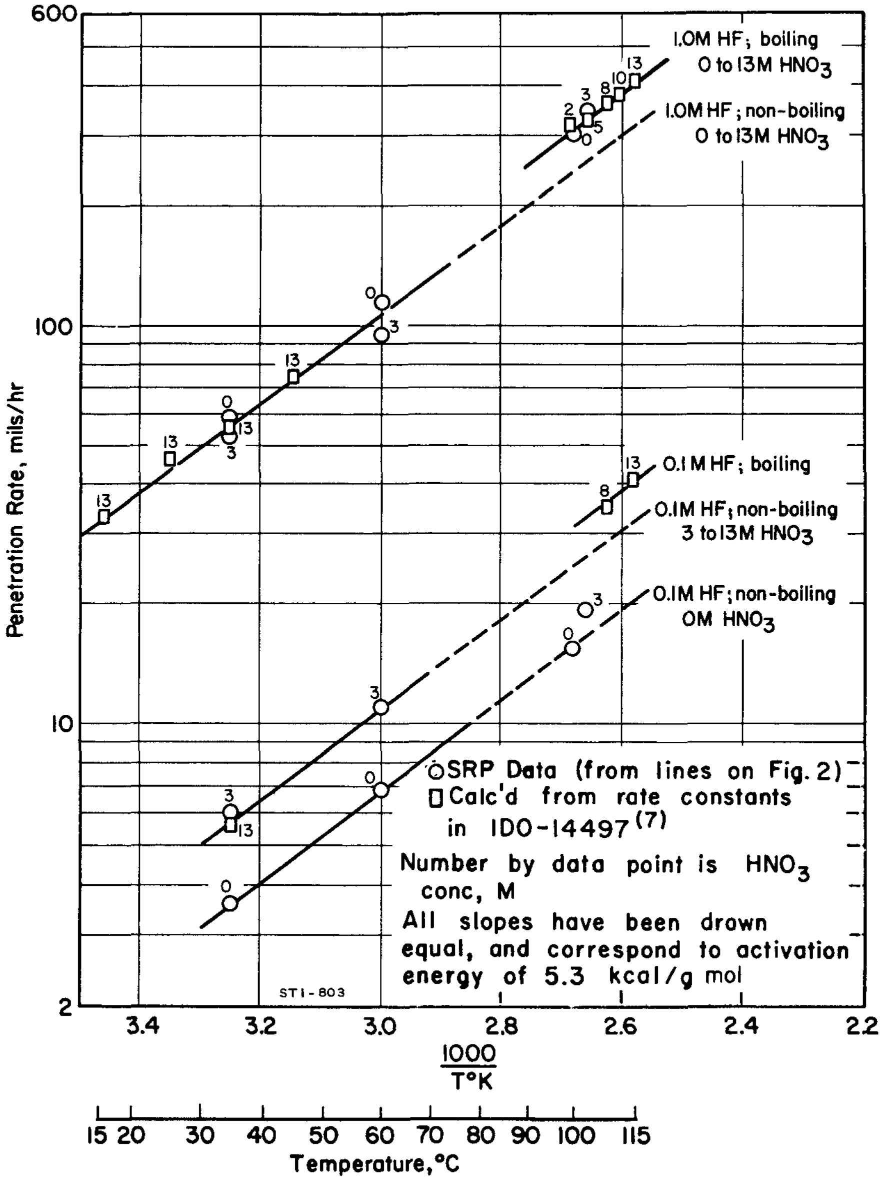

FIG. 4 DISSOLUTION RATES OF ZIRCONIUM AND ZIRCALOY-2 IN HF-HNO_3: TEMPERATURE AS CONTINUOUS VARIABLE

CORROSION STUDIES

Method of Measurement

Corrosion rates of 304L and 309SCb stainless steels were measured by determining the loss in weight of samples of known surface area in solutions containing HF, HNO_3, Al, U, and Zr (method described in DP-486[3]). To conform with equipment in the separations plant at Savannah River, wrought 304L was "Heliarc"* welded with 308L filler rod, and 309SCb was metal-arc welded with 309SCb filler rod.

Liquid Phase

The corrosion tests were conducted in a "Teflon"-lined vessel, 1-3/4 inches in diameter and 12 inches high; a glass reflux condenser was used for tests at the boiling point.

The corrosion rates of both welded and wrought 309SCb stainless steel in boiling mixtures of HF-HNO_3 pass through minimum values as the nitric acid concentration is increased from zero up through 0.5M, at constant hydrofluoric acid concentration (Figure 5). In contrast, the rates of corrosion at constant nitric acid concentration increase without minima as the hydrofluoric acid concentration is increased (Figure 6). Metal-arc welds of 309SCb are preferentially attacked in boiling mixtures containing nitric acid, although the attack is not pronounced until the concentration exceeds 1.0M (Figure 7).

The effect of temperature on the corrosion rate of 309SCb stainless steel is shown in Figure 8; for several concentrations of hydrofluoric and nitric acids, an activation energy of 13.3 kcal/(g mol) was calculated from the slope of the lines shown. Most of the points on Figure 8 were taken from lines drawn through the experimental data on Figure 9. The latter illustrates the effect of hydrofluoric acid concentration on the corrosion rate of 309SCb, with temperature and nitric acid concentration as parameters. The most significant feature of the corrosion versus temperature relationship on Figure 8 compared to the relationship for zirconium dissolution on Figure 4 is that lowering the temperature decreases corrosion of 309SCb stainless steel more than it decreases the dissolution of zirconium.

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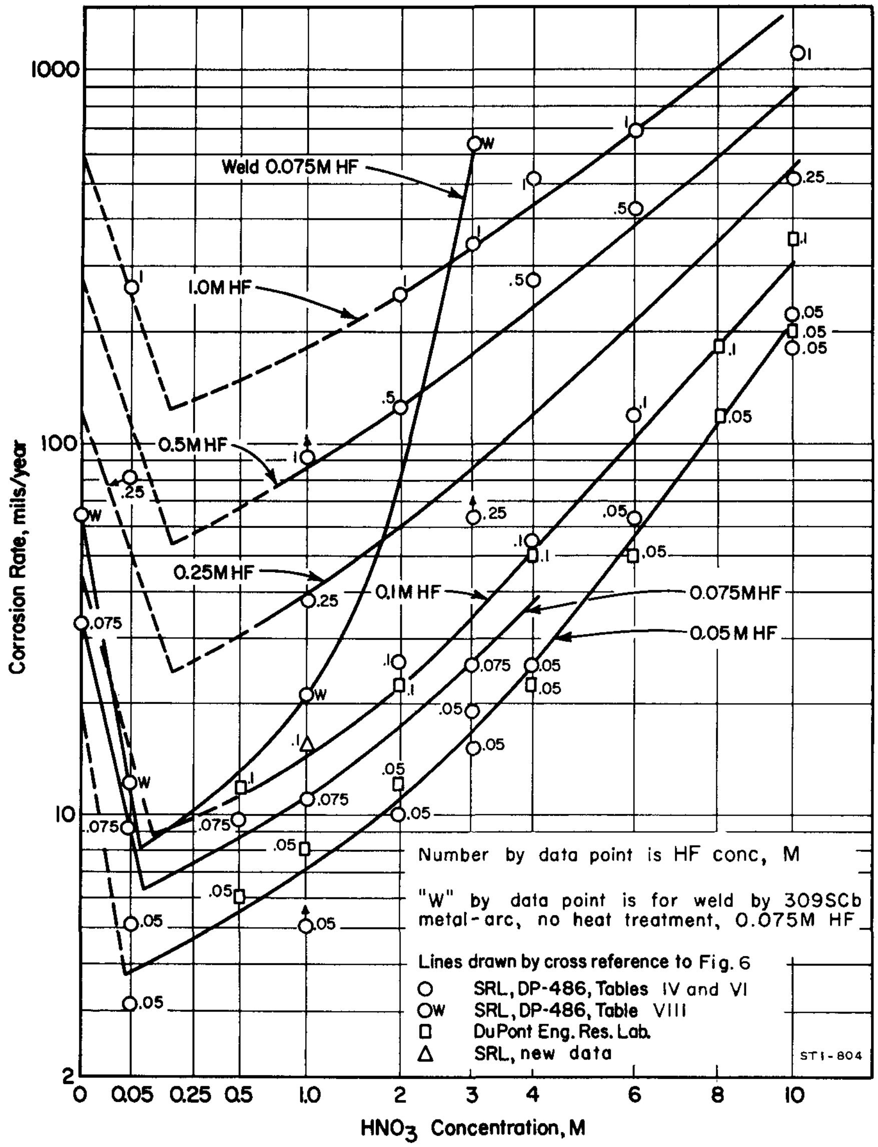


FIG. 5 CORROSION RATE OF 309SCb STAINLESS STEEL IN BOILING HF-HNO_3: HNO_3 CONCENTRATION AS CONTINUOUS VARIABLE

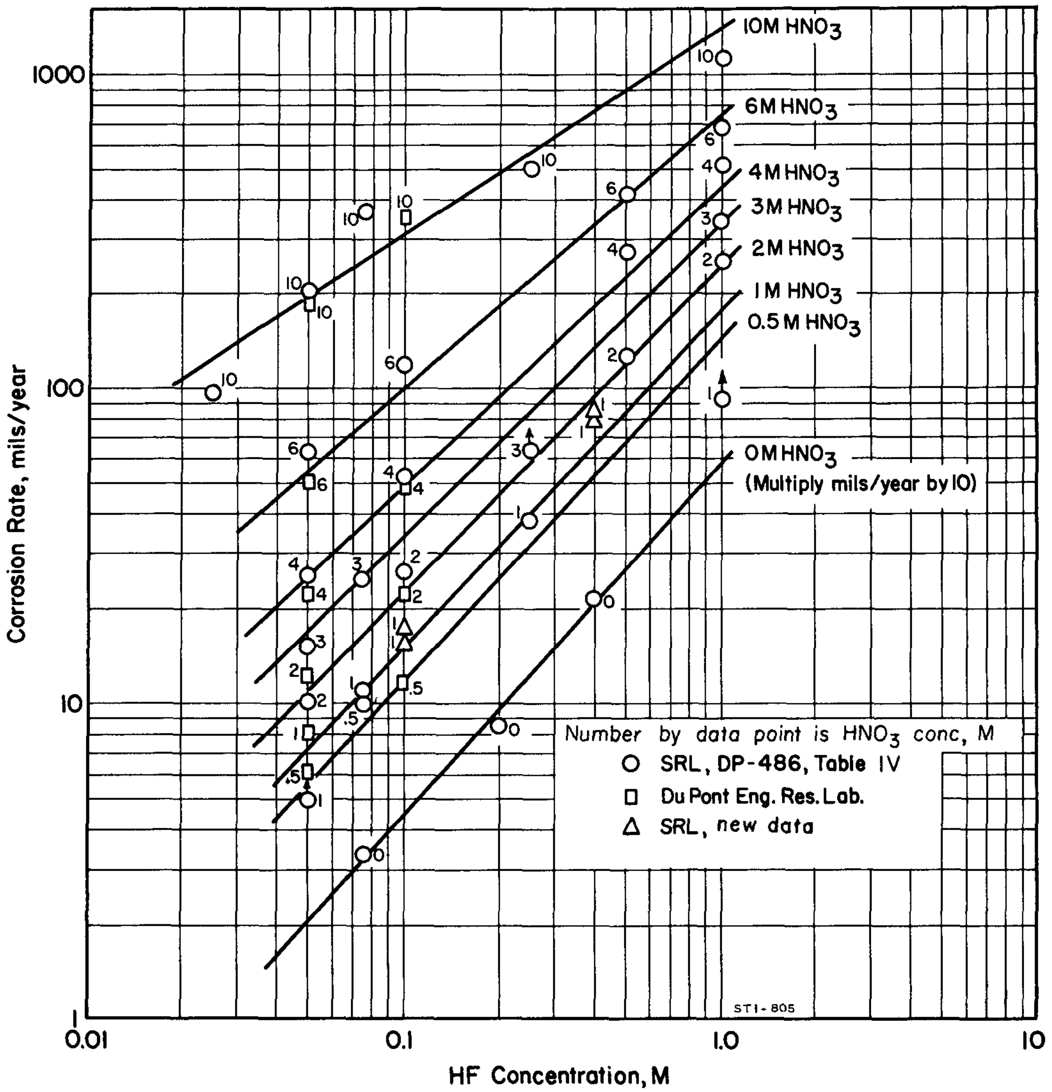


FIG. 6 CORROSION RATE OF 309SCb STAINLESS STEEL IN BOILING HF-HNO$_3$: HF CONCENTRATION AS CONTINUOUS VARIABLE

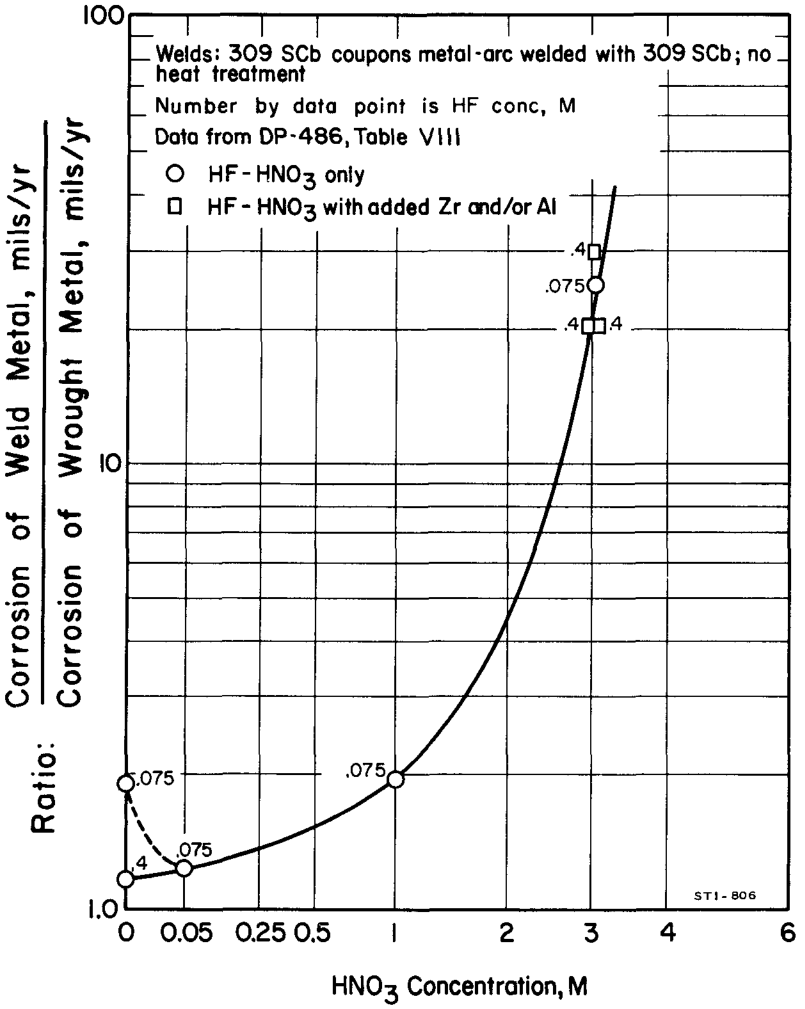
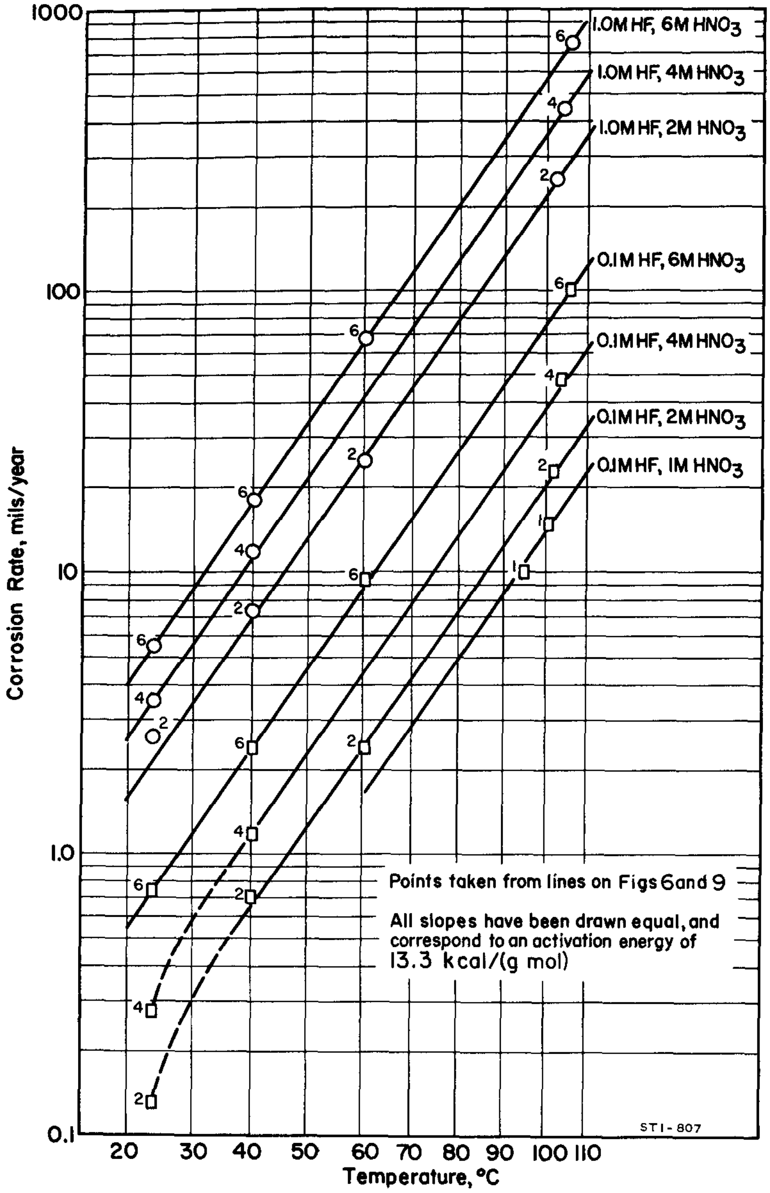


FIG. 7 INCREASE IN CORROSION OF 309SCb STAINLESS STEEL WELDS RELATIVE TO WROUGHT METAL



Points taken from lines on Figs 6 and 9

All slopes have been drawn equal, and correspond to an activation energy of 13.3 kcal/(g mol)

FIG. 8 CORROSION RATE OF 309SCb STAINLESS STEEL IN HF-HNO$_3$: TEMPERATURE AS CONTINUOUS VARIABLE

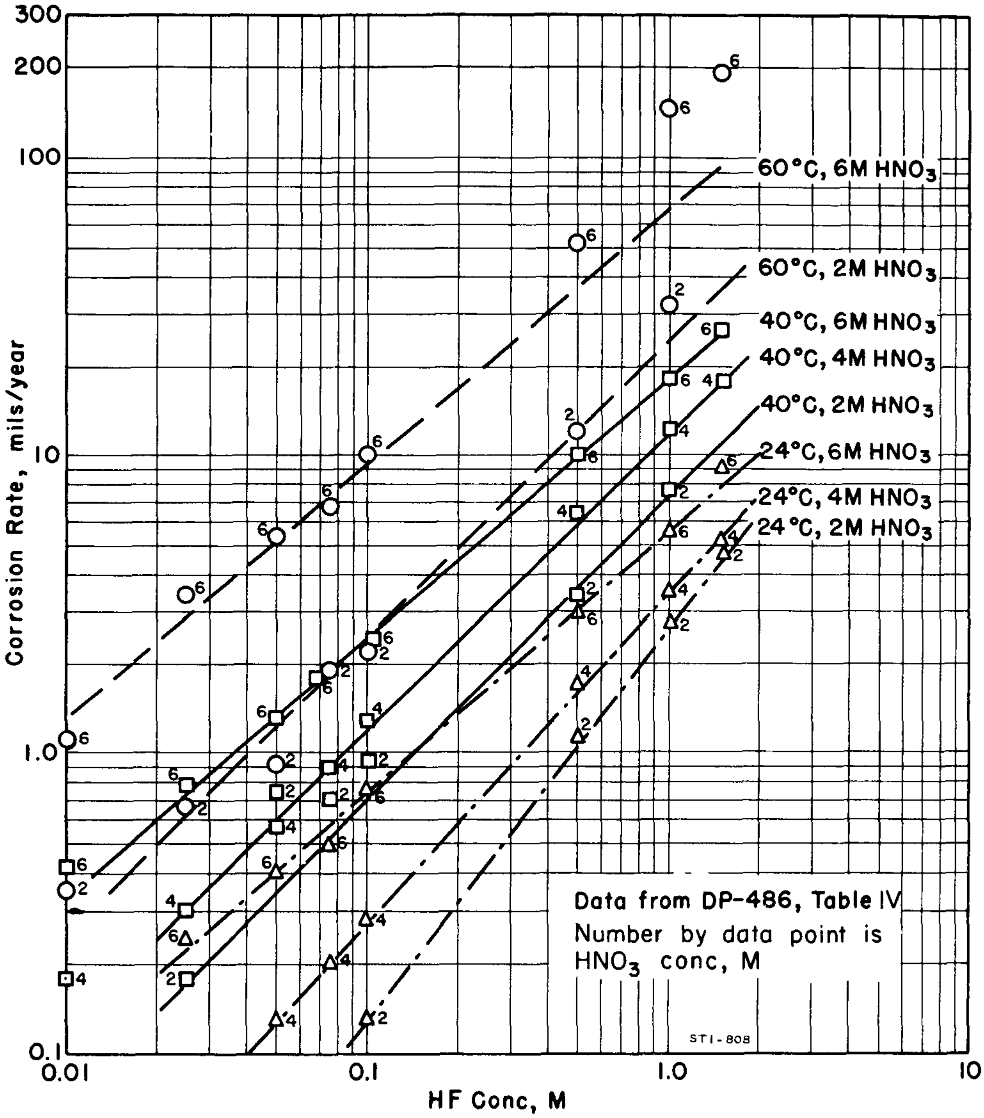


FIG. 9 CORROSION RATE OF 309SCb STAINLESS STEEL IN HF-HNO$_3$ AT 24, 40, AND 60°C: HF CONCENTRATION AS CONTINUOUS VARIABLE

Vapor Phase

The corrosion of 309SCb stainless steel was measured in the vapor phase above mixtures of HF, HNO_3, and Zr at various boilup rates (Table I). A boilup rate of 1.3 g/(hr)(cm^2) approximates that expected during plant-scale dissolution. Test coupons placed in the vapor phase of the equipment are actually exposed to a mixture consisting of condensate from the reflux condenser, entrainment, and dry vapor from the boiling liquid. Corrosion rates of 309SCb stainless steel in the vapor phase are considerably less than in the liquid phase at plant boilup rates.

Since inexplicably high rates of corrosion in the vapor phase were measured at the high boilup rates (Table I), an experiment was undertaken to clarify the results. A 10% fraction of the dissolver solution was removed by single-stage distillation from a mixture of 1M HNO_3, 2.6M HF, and 0.5M Zr and used for corrosion tests of 309SCb. The corrosion rates in both the boiling liquid and the vapor phase of this fraction were below the limits of measurement. It was concluded that the high corrosion rates in the vapor phase at the high boilup rates were caused by entrained salt that concentrated on the test coupon. This conclusion is corroborated by data from the low-boilup experiments: when an air sweep was used, the corrosion rate of samples in the vapor phase was greater than without the air sweep, presumably because of faster concentration by evaporation of the small amounts of entrainment.

TABLE I

Effect of Boiling and Air-Sweep Rates on Corrosion Rate of 309SCb Stainless Steel by 1.0M HNO_3 and Fluoride

HF, M	Zr, M	Temp, °C	Boilup(a)	Air Sweep, cc/(hr)(cm^2)	Corrosion Rate, mils/yr	
					Liquid	Vapor
0.1	0	95	None	0	10	1
0.1	0	95	None	385	10	1
0.1	0	BP(b)	Low	0	16	1
0.1	0	BP	Low	385	14	2
0.4	0	BP	Low	0	83	6
1.1	0.2	95	None	0	19	1
1.1	0.2	95	None	385	17	3
1.1	0.2	BP	Low	0	30	1
1.1	0.2	BP	Low	385	27	7
0.1	0	BP	High	0	17	8
0.4	0	BP	High	0	77	112
1.0	0.15	BP	High	0	52	78
1.1	0.2	BP	High	0	34	57
2.0	0.4	BP	High	0	59	147
3.0	0.65	BP	High	0	43	282

(a) Low boilup = 1.3 g/(hr)(cm^2); high boilup = 13 g/(hr)(cm^2)
(b) BP = boiling point

DISSOLUTION PROCEDURE FOR Zr – LOW U FUEL ELEMENTS

The Zr – low U alloys can be dissolved at 60°C or lower by continuously feeding concentrated hydrofluoric acid to the dissolver through a "Hastelloy" F* line that extends below the liquid level. Agitation is necessary since operation is below the boiling point. The hydrofluoric acid should be added at a uniform rate throughout the dissolution period. The rate of addition is chosen to give a rate of reaction that does not exceed the heat-removal and off-gas capacity. For complete dissolution, 5 mols of hydrofluoric acid must be added for each mol of zirconium charged. Clear and stable dissolver solutions, prepared by dissolving unirradiated Zr – low U fuel on a laboratory scale, contained about 0.5M Zr, 0.4M NO_3^-, and 2.5M HF.

The preferential attack of HF-HNO_3 solutions upon metal-arc welds of 309SCb stainless steel is very dependent upon nitric acid concentration; 1M HNO_3 appears to be the optimum concentration when dissolving in 309SCb stainless steel equipment. In practice hydrofluoric acid is added to a solution that is initially 1M in nitric acid; the final nitric acid concentration will be about 0.4M. The quantity of fuel charged is adjusted to yield a solution of about 0.5M Zr.

In Figure 10 the dissolution rate of Zircaloy-2 is compared with the corrosion rate of 309SCb welds under a variety of conditions. The ratio between dissolution rate and corrosion rate at a given temperature does not change with changes in hydrofluoric acid concentration; that is, an increase in hydrofluoric acid concentration accelerates both processes to the same degree. Consequently whether hydrogen fluoride concentration leads to fast or slow dissolution, the amount of vessel corrosion remains proportional to the thickness of Zircaloy penetrated, and thus to the number of charges dissolved. Furthermore, the ratio of dissolution to corrosion is not influenced by disappearance of fluoride to form a complex with dissolved zirconium, since both rates are affected equally.

Solutions downstream from the dissolver at Savannah River are processed in equipment made of 304L stainless steel. Typical solutions would contain HF, HNO_3, U, and Zr, with Al added to complex the free fluoride remaining after zirconium dissolution. (Uranium has been found to have little effect on corrosion(4). The fluoride complexing powers of several cations are described in ORNL-2713(5).) The rate of corrosion of wrought 304L welded with 308L in typical aluminum-containing

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*"Hastelloy" is a trademark of Haynes Stellite Co., Division of Union Carbide Corp., Kokomo, Ind.

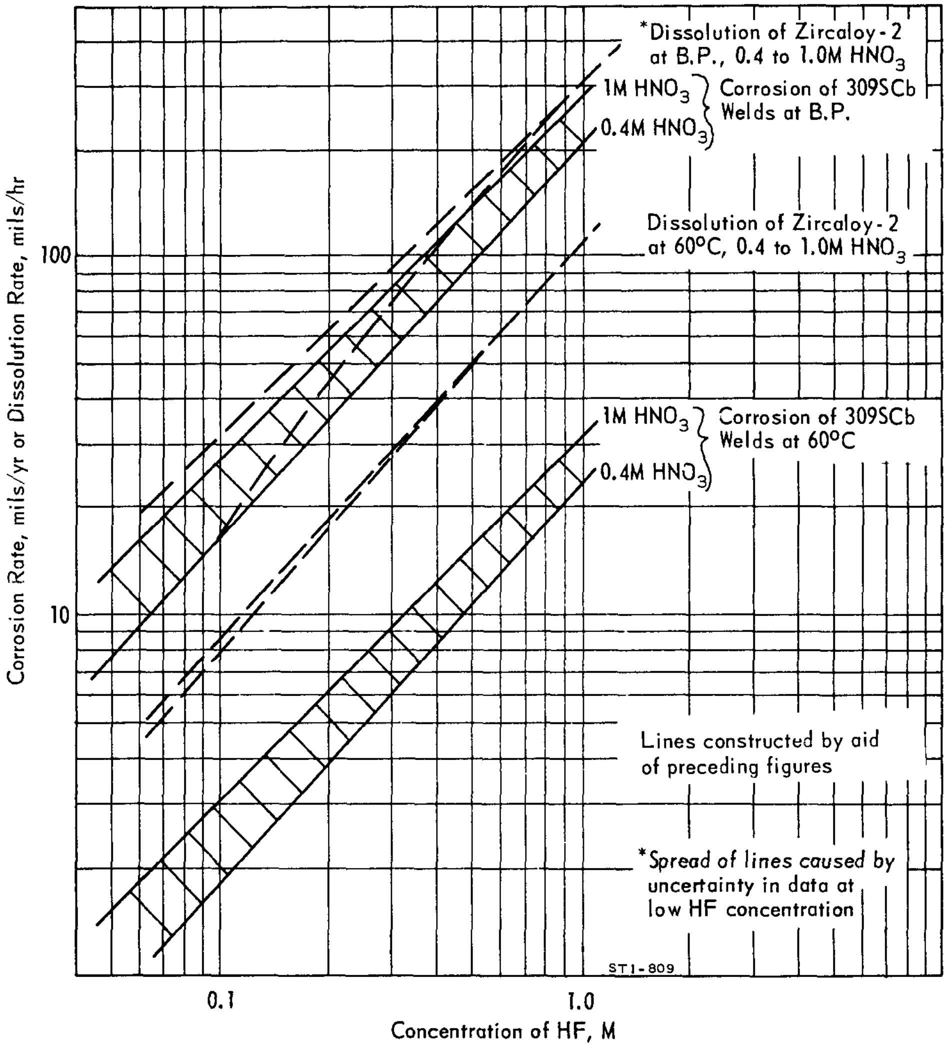

FIG. 10 DISSOLUTION OF ZIRCALOY - 2 AND CORROSION OF 309SCb STAINLESS STEEL WELDS IN HF - HNO_3

solutions at 40°C is less than 10 mils/yr(3). Boiling solutions containing uncomplexed fluoride are very corrosive to 304L stainless steel and have been used to dissolve 304L cladding(2). Even at 40°C, the corrosion rate with the uncomplexed fluoride is 200 to 500 mils/yr.

During a typical dissolution of Zr — low U fuel the average composition of the off-gas downstream from the reflux condenser was 8% H_2, 18% N_2, 50% NO, 23% N_2O, and 1% miscellaneous gases. The nitric acid not only reduces the corrosion of wrought and welded 309SCb stainless steel (Figure 5), but also suppresses the evolution of hydrogen from the reaction of zirconium with hydrofluoric acid. Air can be used to dilute the off-gas to less than 4% H_2. The air flow rate required depends upon the maximum surface of metal exposed during dissolution. If a penetration rate of 10 mils/hr and a gas evolution rate of 1.5 mols per mol of zirconium dissolved are assumed, the maximum off-gas rate per square foot of surface is about 0.033 SCFM (standard cubic feet per minute).

SEMIWORKS TESTS

The successful dissolution of Zircaloy-2 plates in boiling 1M HNO_3 to which concentrated hydrofluoric acid was slowly added is described in DP-519(6). A 27.5-lb charge was dissolved in 12.5 hours. The free fluoride did not exceed 0.12M, and the corrosion rate of 309SCb stainless steel coupons was 25-30 mils/yr.

A fuel element made of four plates of Nb-U alloy clad with Zircaloy-2 was used to demonstrate dissolution below the boiling point (the Nb-U element was the only type available at the time). The test plates were 4.5 ft long and 1.4 inches wide, and were aligned with a plate-to-plate clearance of 70 mils. Autoclaving had left a tight, black film of oxide on the surface.

The element was submerged in 1M HNO_3 at 70°C, and the acid was circulated through the housing by the steam jet at 2 gal/min (1 ft/sec within the small clearance between plates). 309SCb metal-arc-welded corrosion coupons were placed in the housing, in the bulk solution, and in the vapor space. Hydrofluoric acid (30M) in excess of the 5 mols per mol of zirconium required was added at a controlled rate directly to the jet suction.

Six runs were made with the hydrofluoric acid addition rate varied between 1 and 2 liters/hr; the fluoride uncomplexed with zirconium varied between 0.4 and 1.2M. As expected, the rate of attack on both Zircaloy-2 and stainless steel increased with higher hydrofluoric acid concentrations; a typical result at low hydrofluoric acid concentration was 18 mils/hour on the Zircaloy-2 and 25 mils/year on the steel. The temperature inside the container at the jet discharge was 80°C, and the rate of corrosion of the coupons in this vicinity was 320 mils/yr (13 times the rate in the bulk liquid). The coupons in the vapor phase corroded at rates of less than 10 mils/yr. As expected, the Nb-U alloy did not dissolve, but the Zircaloy-2 cladding and edge guides disappeared in 3.5 to 7 hours, depending on the hydrofluoric acid concentration. Inspection after one hour of exposure showed that the cladding had not been appreciably attacked, although the edge guides were dissolving. Subsequent laboratory tests showed that the black oxide film on the surface of the Zircaloy-2 was not attacked for about 1.5 hours; in contrast, the edge guides, which had been machined after autoclaving, had no protective film to delay the attack. This 1.5-hour induction period added 15-20% to the time cycle.

The tests showed that the Zircaloy-2 dissolved 4000 to 6000 times as rapidly as the stainless steel corroded; this ratio is satisfactory. The data indicate that instantaneous rates of corrosion between 25 and 50 mils/yr may be expected in the plant dissolvers. In practice, about 300 kg of zirconium will be dissolved in a typical cycle of 10 to 12 hours, so that less than 1 mil would be corroded from the most sensitive parts (the welds) of the dissolver for every 10 tons of zirconium fuel dissolved.

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