CORROSION OF BORON-STAINLESS STEEL
BY NITRIC ACID

by

D. S. Irwin

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ABSTRACT

A study was made of the corrosion of boron-stainless steel by nitric acid solutions. The rates of boron loss due to thickness reduction and leaching of the remaining metal were determined. The data were extrapolated to calculate the useful life of boron-stainless steel as a neutron poisoning agent.

SUMMARY

A study was made of the corrosion of boron-stainless steel coupons by nitric acid solutions. The boron loss, because of reduction in thickness and by leaching from the base metal, was determined as a function of time. It was found that leaching removed more than four times as much boron as was removed by thickness reduction. It was concluded, therefore, that thickness measurements only, are not a reliable guide to the integrity of a boron-stainless steel neutron poison. Using the data obtained, the useful life of the neutron poison in the experimental plutonium anion exchange column was found to be about 4 years.

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INTRODUCTION

An experimental 18-in. diameter anion exchange column was built and tested for use in plutonium purification. Use of a neutron poison permitted the experimental column diameter to be 18 in. rather than the 6-in. maximum safe diameter permitted for non-poisoned plutonium anion exchange equipment.

Neutron poisoning was accomplished by a boron-stainless steel gridwork placed in the ion exchange resin bed. The grid plates were rolled from Type-304L stainless steel which contained approximately 1-percent boron by weight. About 90 percent of the boron was the boron-10 isotope. The thickness of the grids was approximately 0.165 inch.

The grids were required to withstand attack by the ion exchange process-liquids that were nitric acid-water solutions of various compositions containing plutonium and other dissolved substances. Any removal of boron from the grids by nitric acid attack would have reduced the nuclear safety of the equipment. Therefore, maintenance of the integrity of the grids was of utmost importance.

When the 18-in. diameter column was put into use, four coupons of the same thickness and chemical composition as the grids were inserted in the resin bed. It was decided to monitor the integrity of the grids by periodically determining the thicknesses of the coupons. Use of this procedure assumed that boron was lost from the coupons only by uniform removal of material from the coupon surfaces and not by leaching from the base material.

A test program was undertaken to determine if the assumption was sufficiently accurate for estimating the quantity of boron remaining in the boron-stainless steel neutron poison.

EXPERIMENTAL

REPARATION OF PHOTOMICROGRAPHS

Photomicrographs of the boron-stainless steel coupons were prepared by

the following procedure:

1. The sample surface was cut normal to the leached surface so that the interface and the body of the metal were exposed in one plane.
2. The surface was sanded and polished. Final polishing was done with 1-micron particles suspended in a paste.
3. The surface was ion bombarded to bring the crystal structure into relief.
4. The surface was photographed at 100, 250, and 500 magnifications.

ANALYSIS FOR BORON

The boron-stainless steel coupons were analyzed for boron by the following procedure:

1. The metal sample was dissolved in hydrochloric acid.
2. The residue from the dissolution was recovered by sodium carbonate fusion and then added to the sample.
3. The cations were removed from the solution by treatment with Dowex 50 resin (sodium form).
4. Mannitol was added to form mannitol-boric acid complex.
5. The complex was titrated with sodium hydroxide.
6. The results were reported as weight percent boron.

THICKNESS DETERMINATION

The coupon thicknesses were determined by use of a Scherr-Tumico micrometer.

DISCUSSION

Ion exchange process solutions which contacted the boron-stainless steel grids were largely of the following two types:

1. A high-nitric-acid-concentration solution which contained moderate amounts of plutonium and other elemental impurities.
2. A low-nitric-acid-concentration solution which contained large amounts of plutonium but very small amounts of other elemental impurities.

The high-acid-concentration solution contacted the grids about 75 percent of the exposure time and the low-acid-concentration solution contacted the grids 25 percent of the exposure time.

Typical average chemical analyses of the solutions are given in Table I. The plutonium and americium levels were determined radiometrically. Other major elemental impurities were determined by emission spectroscopy. These solutions contacted the ion exchange resin and grids at temperatures of 25 - 50°C under both static and flowing conditions.

TABLE I

Typical Average Chemical Analyses of Nitric Acid-Water Solutions

Elemental Analyses, mg per liter

Nitric Acid Normality	Pu	Am	Al	Ca	Cr	Cu	Fe	K	Mg	Mn	Mo	Ni	Pb
7.5	1,500	5	2	50	25	20	600	800	20	10	5	15	35
0.35	20,000	<1	<1	2	<20	<1	20	5	3	<1	<3	<2	1

Data are presented in Table II showing the change in coupon thickness, as a function of time, from being in contact with the chemical solutions. After the original measurement, no data are given until the total contact time reached 154 days. This was because the measurements taken prior to 154 days were found to be inaccurate. The inaccuracy was apparently because of acid vapor attack on the micrometer.

TABLE II

Thickness Measurements of Boron-Stainless Steel Coupons

Coupon No.	Original Thickness, (in.)	Thickness After 154 Days, (in.)	Thickness After 197 Days, (in.)	Total Loss (in.)
1	0.165	0.1645	0.163	0.002
2	0.165	0.165	0.165	0.000
3	0.165	0.164	0.162	0.003
4	0.163	0.161	0.161	0.002

Table II shows that after being in contact with the acid process solutions for almost 200 days, the average thickness-loss of the coupons was less than 0.002 inch.

Boron analyses of the coupons yielded more significant results than thickness measurements. After being in contact with the acid, for 105 days, small samples were cut from each of the four coupons and from the original metal. A part of each sample was submitted to the Rocky Flats Metallography Laboratory for examination. The remaining part was analyzed by the Plutonium Laboratories for boron content.

Results of the boron analyses are shown in Table III. Duplicate determinations were made on three samples. The first sample consisted of the unleached original metal. The second and third samples were fractions of the leached coupons. The outside fraction consisted of 0.082 in. of metal cut from the surfaces of each of the four coupons. The inside fraction was the metal remaining after the outside fraction was removed.

The results show that, when compared with the original metal, the inside fraction was not depleted in boron. However, approximately 7 percent of the boron from the outside fraction was leached away by the acid environment.

TABLE III

Boron Analyses of Metal Coupons

Sample Description	Boron Analyses, w%	Average Boron Analysis, w%
Original Metal	1.02 1.04	1.03
Outside Fraction After 105 Days in Acid	0.96 0.97	0.965
Inside Fraction After 105 Days In Acid	1.03 1.05	1.04
Metal After 197 Days in Acid	1.01 0.95	0.98

Figure 1 is a photomicrograph of the original metal used in construction of the grids. At the left side of the photograph the air-metal interface may be indistinctly seen. This photograph and those in Figure 2 were taken at a magnification of 250X.

Figure 2 shows each of the four leached coupons. The interfaces are more distinguishable than in Figure 1. It should be noted that the microstructure of the original metal is very different from that of the coupons. The chips and scraps, generated when the grids were built, were melted and recast. The coupons were fabricated from the recast material. The recrystallization evidently caused the significant differences in microstructure between the coupons and the grid material.

Figure 1. PHOTOMICROGRAPH OF ORIGINAL (UNLEACHED) BORON-STAINLESS STEEL - X250

The microstructures are thought by Metallography Laboratory personnel to consist of primary crystals of metastable austenite in boron-rich eutectic matrices. The white areas are the primary crystals and the dark areas are the boron-rich phase. These photographs indicate that the boron-containing material is preferentially leached out of the base metal. The boron leaching data in Table III substantiates this observation. These findings agree with work published previously by F. E. Butler.⁽¹⁾

The question arises as to the adequacy of using the condition of metal of one microstructure, such as coupons, to predict the corrosion rate of metal of the same composition but a different microstructure, such as the grids. Butler⁽¹⁾ published data on the corrosion rates of the original and re-melted metal in 7N nitric acid solutions which contain small amounts of aluminum-complexed fluoride ion. This solution composition approximates that experienced by the grids and coupons in the grid ion-exchange column. It is shown that both microstructures suffer corrosion of the same order of magnitude, but that the metal of the coupons appears to corrode more rapidly than the grid metal. Therefore, determining the condition of the

(1) Butler, F. E., Corrosion Studies on 304 Stainless Steel Containing one percent Boron-10, The Dow Chemical Company, Rocky Flats Division, July 19, 1963, RFP-307.

No. 1

No. 2

No. 3

No. 4

Figure 2. PHOTOMICROGRAPHS OF LEACHED BORON-STAINLESS STEEL COUPONS - X250

grids by the condition of the coupons affords a factor of safety for clear safety judgments.

Another boron-analysis was made after the coupons were in contact with the acid solutions for 197 days. Cross-sectional cuts were taken from each coupon and duplicate analyses were made of the total sample. These results are presented in Table III.

The results show a progressive leaching of the boron from the base material. The average boron content of the original metal was 1.03 w%. The average after 105 days was 1.00 percent. The average after 197 days was 0.98 percent. These results indicate a significant boron loss beyond that detectable by the thickness measurements.

The data given in Tables II and III are presented graphically in Figure 3. In addition, a curve is plotted which represents the total equivalent loss of boron due to leaching and thickness reductions.

Figure 3. LOSS OF BORON FROM COUPONS

Figure 3 shows that the majority of the boron-loss results from leaching. Therefore, thickness measurements are of little value in a nuclear safety program such as this.

Using the information from Figure 3, the useful life of the grids was predicted. In the original criticality tests, the 18-in. diameter ion column was found to be safe when using 0.090-in. thick grids. The column, however, was built with 0.165-in. thick grids; therefore, the grids could lose 0.075 equivalent inch of material ($0.165 - 0.090$) before being considered unsafe. Assuming that boron loss would have continued at the average rate (average of the first 197 days) the grids would have lasted for a total of 3.8 years. If the calculation is made on the basis of the slope of the total loss curve of Figure 3 at 197 days, the useful life becomes 4.7 years.

No further data on grid corrosion were obtained to confirm or refute these results because the grid column was found to be economically infeasible and was scrapped.