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CORROSION STUDIES PERTINENT TO BROMINE TRIFLUORIDE PROCESSES

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2

TABLE OF CONTENTS

Page

I. INTRODUCTION 3

II. CORROSION OF VARIOUS METALS BY BROMINE TRIFLUORIDE SOLUTIONS 5

  A. Static Refluxing Tests 5

  B. Corrosion in Bromine Trifluoride Condensate 7

III. CORROSION OF SILVER SOLDER 10

IV. AQUEOUS CORROSION OF MONEL 15

  A. Aluminum Nitrate Solution Corrosion 15

  B. Sulfamic Acid Inhibition of Nitrate Corrosion 17

V. CORROSION OF MONEL EXPOSED ALTERNATELY TO BROMINE TRIFLUORIDE AND CERTAIN AQUEOUS SOLUTIONS 25

3

CORROSION STUDIES PERTINENT TO BROMINE TRIFLUORIDE PROCESSES

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J. G. Schnizlein, R. K. Steunenberg and R. C. Vogel

ABSTRACT

The corrosion rates of certain metals and alloys have been determined in several solutions typical of bromine trifluoride processes. Nickel, Monel and K. Monel showed excellent corrosion resistance in the following solutions at 125° C: bromine trifluoride, ten mole per cent bromine in bromine trifluoride, ten mole per cent bromine pentafluoride in bromine trifluoride, and ten mole per cent uranium hexafluoride in bromine trifluoride. Inconel and Duranickel also proved satisfactory. Stainless steel, mild steel, magnesium and aluminum are suitable for less critical applications. Nicloy-9 was totally unsatisfactory.

Among the silver solders tested, American Platinum Works Silvaloy 355 far excelled the others in its corrosion resistance toward bromine trifluoride. Its use is appropriate in the assembly of laboratory apparatus.

The corrosion rate of Monel in aqueous aluminum nitrate solutions exhibited a strong pH dependence, especially in the tests at higher temperatures. It was also observed that prior contact with bromine trifluoride reduced the corrosion of Monel by aluminum nitrate solutions. The addition of small amounts of sulfamic acid to the aluminum nitrate solution markedly inhibited the corrosion of Monel at low pH values and a temperature of 70° C. This effect persisted up to four days, depending upon the initial sulfamic acid concentration.

Tests on the high nickel alloys (nickel, Monel, K. Monel and Inconel) subjected alternately to bromine trifluoride and aqueous aluminum nitrate solutions showed penetrations of 4 to 5 x 10^{-3} mil per cycle.

I. INTRODUCTION

These corrosion studies were undertaken in order to orient properly the development of processes using bromine trifluoride. Such a process has been contemplated for the separation of uranium and fission

4

products from spent fuels from nuclear reactors.[1] These studies are limited to static tests; therefore cases involving flow, stress, crevices, etc., should be examined more carefully.

Qualitative and semi-quantitative data of the corrosion of certain metals by halogen fluorides had shown alloys of high nickel content to be most suitable for small-scale, semi-permanent laboratory equipment. For pilot plant and full-scale equipment, however, the questions of cost and equipment life required more careful determinations of corrosion by bromine trifluoride solutions. Corrosion tests up to 20 weeks in duration were conducted on the high nickel alloys and a few other common metals at 125° C in four bromine trifluoride solutions (pure, 10 mole per cent bromine, 10 mole per cent bromine pentafluoride, and 10 mole per cent uranium hexafluoride). The experimental results and descriptions of the equipment and procedures are presented in Section II.

Since it is more convenient to use silver solder for joining components than heliarc welding, the corrosion of various silver solders in bromine trifluoride was investigated. Although the study was not as extensive as that above, the data presented in Section III clearly show the superior resistance of Silvaloy 355 (American Platinum Works).

One scheme of processing plutonium-uranium alloys by a fluoride volatility method suggests that plutonium and fission product fluorides be removed from the Monel or nickel vessel by washing with an aqueous aluminum nitrate solution. It was, therefore, appropriate to investigate the corrosion of these materials under these circumstances. The study of the corrosion of Monel in aluminum nitrate solutions is presented in Section IV. It was hypothesized that nitrous acid is an intermediate in the corrosion mechanism. This hypothesis offered the possibility of inhibiting corrosion by nitrous acid removal through additions of sulfamic acid, ferrous sulfamate, urea or other similar reagents. It was found that sulfamic acid was the most effective additive. A study of its effectiveness and the influence of pertinent variables is presented in Section IV. Most of the tests were of short duration because the aluminum nitrate solution would be used only as a wash.

Since a process vessel might be subjected alternately to interhalogen and aqueous solutions, the high nickel alloys were tested under cyclic conditions similar to those planned for a dissolver. These data are presented in Section V.

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[1] Hyman, H. H., R. C. Vogel, and J. J. Katz, "Decontamination of Irradiated Reactor Fuels by Fractional Distillation Processes Using Uranium Hexafluoride," Paper 546, International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland (July 7, 1955).

5

II. CORROSION OF VARIOUS METALS BY BROMINE TRIFLUORIDE SOLUTIONS

A. Static Refluxing Tests

1. Apparatus

The long-term corrosion tests were conducted in nickel boilers constructed of 3-inch nickel pipe, 12 inches long, with attached air-cooled condensers (see Figure 1). Temperature regulators were installed to prevent an unexpected increase in temperature. A gauge and manifold system permitted pressure measurement and control.

The boiler, containing 450 ml of halogen fluoride, was heated by means of asbestos-covered Nichrome wire wound around the lower half of the boiler. The vapor from the upper portion passed through the side arm to the condenser. Condensate was returned to the bottom of the boiler. The temperature was maintained at 125 ± 5° C.

The metal coupons, previously cleaned by the method described below, were held in a nickel rack (see Figure 2) by Teflon insulators to prevent electrical couples. Nickel, Monel, K Monel, Inconel, welded nickel, and welded Monel were tested in the first series; Duranickel, Incoloy, aluminum, magnesium, stainless steel, mild steel, and Nicloy-9 were tested in the second. The coupons were supported in the liquid, at the liquid-vapor interface, and in the vapor space.

Four different bromine trifluoride solutions were tested (pure, 10 mole per cent bromine, 10 mole per cent bromine pentafluoride, and 10 mole per cent uranium hexafluoride). The pressure over each of these systems was different, but the method of operation and the temperature were the same.

2. Coupon Preparation

Squares (1-1/2 inch) were sheared from 1/16-inch sheets of the materials to be tested. To eliminate the stress area of the shear, 1/16 inch was milled from all four edges. In the pre-exposure treatment the 1 3/8 x 1 3/8 x 1/16-inch coupons were polished for one minute with a paste of water and scouring cleanser supported on a pad of fine (000) steel wool using a drill press. The coupons were then washed with water, rinsed with distilled water, then acetone, dried in an oven at 110° C, allowed to cool, and weighed. The coupons were supported between the Teflon spacers in the rack (see Figure 2) and arranged so that each of three sets in the boiler were respectively in the liquid, at the liquid-vapor interface, and in the vapor space.

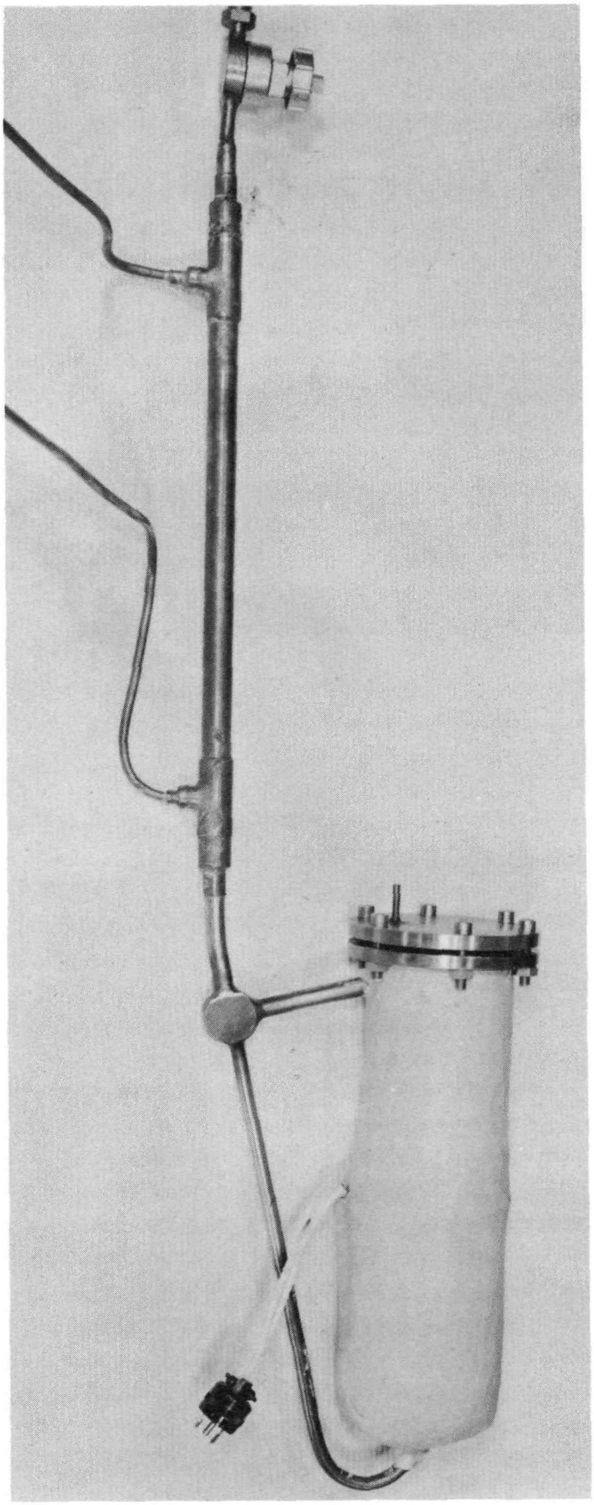

FIGURE 1

CORROSION BOILER FOR INTERHALOGEN SYSTEM

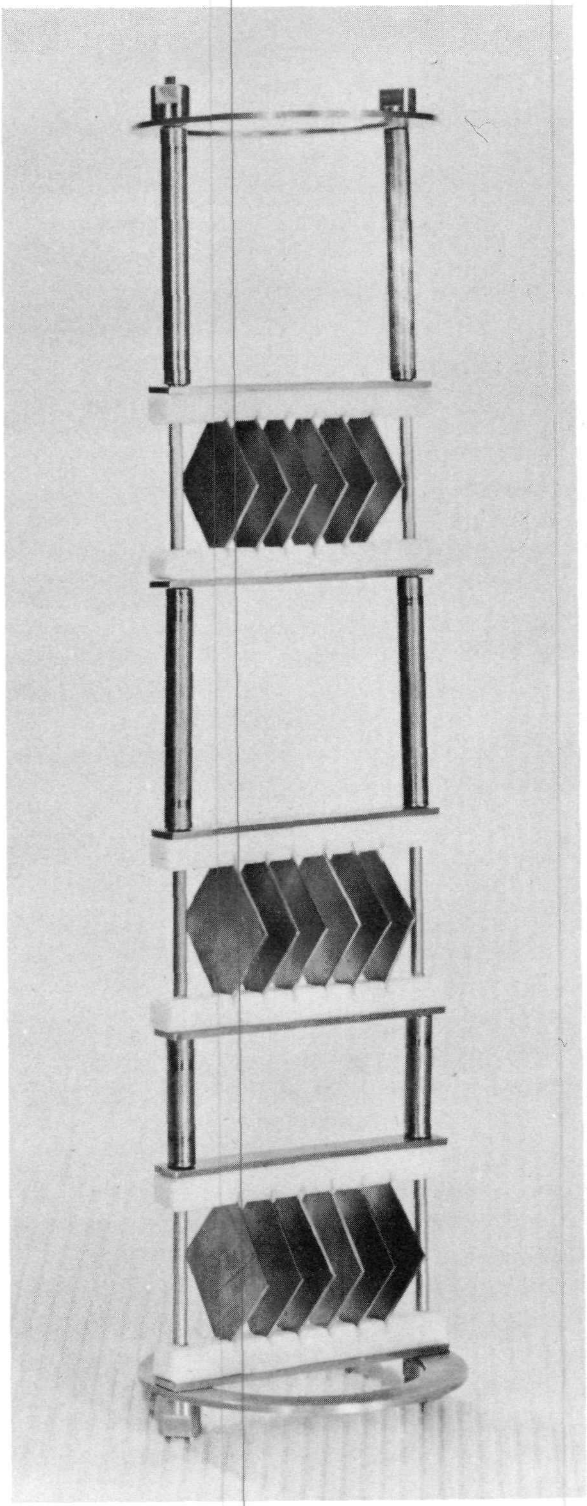

FIGURE 2

COUPON ARRANGEMENT IN CORROSION BOILERS

The halogen fluoride was refluxed at 125° C for a given period of time in the boiler. After removing the coupon rack from the boiler and allowing excess interhalogens to drain off and evaporate, the rack was further dried in an oven at 110° C. The rack and coupons were cooled, disassembled and the coupons were weighed. The weights of the high nickel alloys were determined after the first, third, seventh, eleventh and, in some cases, twentieth weeks of exposure. The other metals were weighed after the first, second, third and fourth weeks. Each coupon was replaced in the rack in its former position and returned to the boiler for additional exposure. Since the interval weights showed no evidence of change of rate with time the exposures were terminated. After the entire series of exposures to the halogen fluorides, the coupons were washed for 1/2 hour in 1 M aluminum nitrate, 0.05 M sulfamic acid solution, pH adjusted to 0.5, to remove the fluoride films. The results of this series of tests are given in Table 1.

3. Discussion

The high nickel alloys showed extremely low corrosion in the interhalogen solutions and are, therefore, excellent materials of construction. Inconel is somewhat less resistant than nickel and Monel. Duranickel, Incoloy and stainless steel are of intermediate value, showing moderate corrosion rates. Although mild steel gave a somewhat larger corrosion rate the difference of cost must be considered to arrive at a satisfactory choice of material. Aluminum, although showing a fairly low corrosion rate under these conditions, suffered considerable attack at a point of leakage on the outside surface of vessels used in the laboratory (see Figures 3 and 4). Evidently the fluoride film hydrolyzes readily in air and the hydrolysis products of bromine trifluoride attack aluminum rapidly. Magnesium might bear further consideration. Nicloy-9 is completely unsatisfactory.

B. Corrosion in Bromine Trifluoride Condensate*

In the corrosion studies of the previous section the corrosion products were allowed to accumulate in the refluxed interhalogen in which the coupons were immersed. Although very low rates of attack were observed, it was necessary to know to what extent the corrosion products in solution might influence the rate. The solubility of nickel fluoride in bromine trifluoride has been reported as about 1 mg per 100 g solution at 25 and 70° C.[2]

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*The work outlined in this section was carried out by W. J. Mecham and I. O. Winsch.

[2] Sheft, I., H. Hyman, and J. J. Katz, "Solubility of Some Metal Fluorides in BrF_3," J. Am. Chem. Soc., 75, 522, (1953).

Table 1

CORROSION IN INTERHALOGEN SYSTEMS AT 125 C

Coupons:	1 3/8 in. x 1 3/8 in. x 1/16 in. initially polished with fine steel wool and scouring cleanser paste, washed, degreased and dried at 110 C.
Supports:	Insulating Teflon spacers.
Fluoride Film Removal:	1 M $Al(NO_3)_3$, 0.05 M sulfamic acid, pH 0.5.

		Penetration in mils per year(a)											
	Time of Exposure	Pure BrF_3(b)			10% BrF_5 - 90% BrF_3			10% Br_2 - 90% BrF_3			10% UF_6(c) - 90% BrF_3		
Metal	(Weeks)	Vapor	Interface	Liquid	Vapor	Interface	Liquid	Vapor	Interface	Liquid	Vapor	Interface	Liquid
Nickel	11	+(d)	+	+	+	0.006	0.012	+	0.002	0.004	0.008	0.018	0.008
Welded Nickel	11	+	0.0004	+	0	0.012	0.005	+	0.001	0.006	0.007	+	0.0008
Monel	11	+	+	0.005	+	0.025	0.029	+	0.020	0.024	0.004	0.003	0
Welded Monel	11	+	+	0.005	0.004	0.029	0.018	+	0.015	0.033	0.005	0.002	0
K Monel	11	0.0002	0.003	0.007	0.009	0.031	0.036	0.008	0.025	0.034	0.005	0.004	0.004
Inconel	11	0.0005	0.010	0.027	0.0008	0.045	0.046	+	0.029	0.041	0.020	0.011	0.015
Duranickel	4	0.12	0.28	0.30	0.23	0.30	0.26	0.30	0.37	0.37	0.05	0.02	.009
Incoloy	4	1.3	3.2	3.6	1.4	1.5	1.7	0.74	1.0	0.9	0.7	1.2	2.5
Aluminum(e)	4	0	0.71	0.70	0.19	0.10	+(f)	0	0.17	+(d)	+	+	+
Magnesium(g)	4	-(h)	-	+	-	-	+	-	-	+	-	-	-
Stainless Steel (Type 304)	1	2.8	3.6	3.4	5.3	6	6.9	1.3	2.0	2.0	2.5	2.9	4.1
Stainless Steel (Type 347)	1										2.4	3.3	5.8
Mild Steel	1	4.9	7.7	7.8	11	16	19	2.7	4.9	4.1	6.8	5.2	9.0
Nicloy-9	1	-	74	-	-	160	-	-	27	-	-	-	-

(a) In cases when the corrosion rate is of the order of less than 0.1-mil penetration per year, the actual numbers carry little significance. They have been included in this data to emphasize the fact that the test demonstrates high resistance; that is, a corrosion rate of 0.001 mil penetration per year for metal A and 0.002 mil penetration per year for metal B does not necessarily mean that A is twice as good as B, but that both metals are entirely satisfactory for service.

(b) The exposure time for pure BrF_3 to nickel through Inconel was 20 weeks instead of 11.

(c) Initial UF_6 concentration in liquid. Removing and replacing samples necessitated some loss of UF_6 so the final UF_6 concentration was 5.1 mole %.

(d) + indicates a weight gain less than 1 mg.

(e) Concentrated HNO_3 wash used to remove fluoride film from aluminum.

(f) Weight gain 7.8 mg total.

(g) No method devised for film removal without attack of coupon. Weight changes are of the same order of magnitude as Duranickel, so penetrations should be of the same order of magnitude.

(h) - indicates no measurement made.

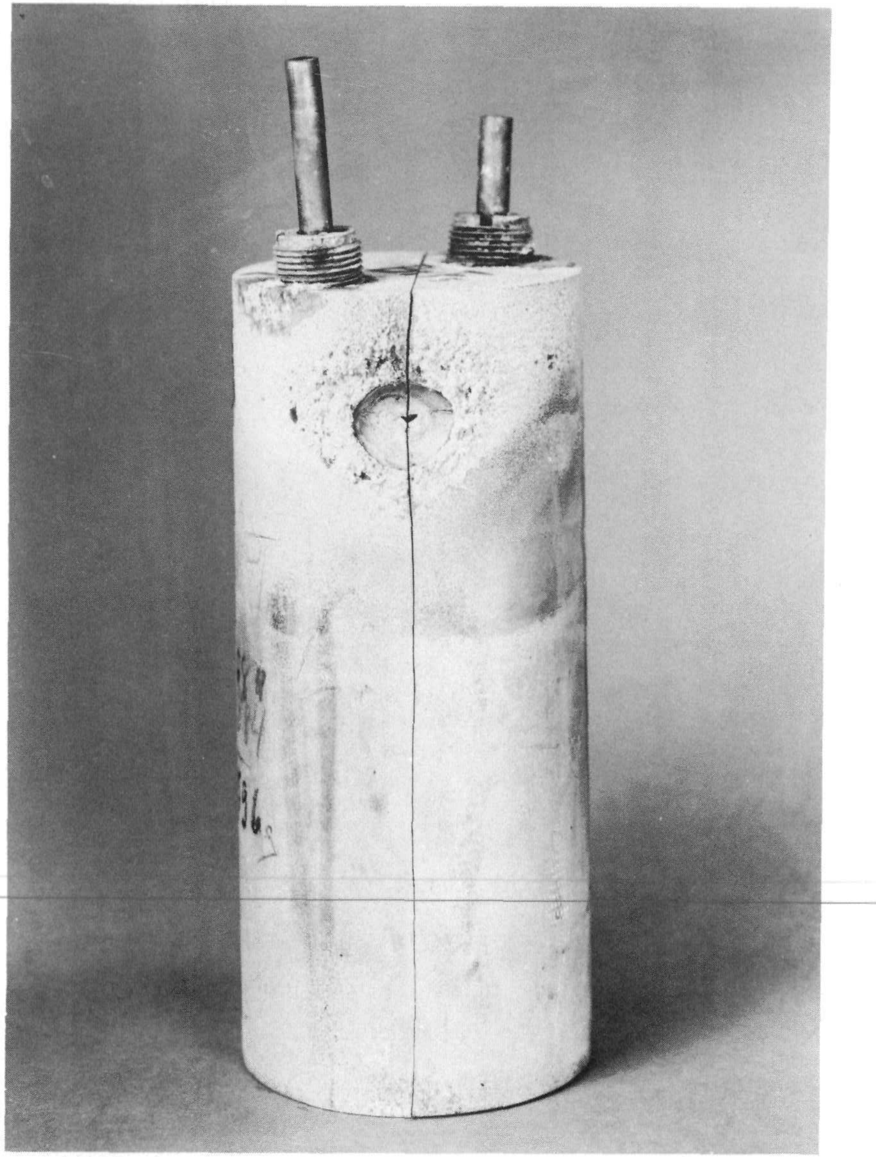

FIGURE 3

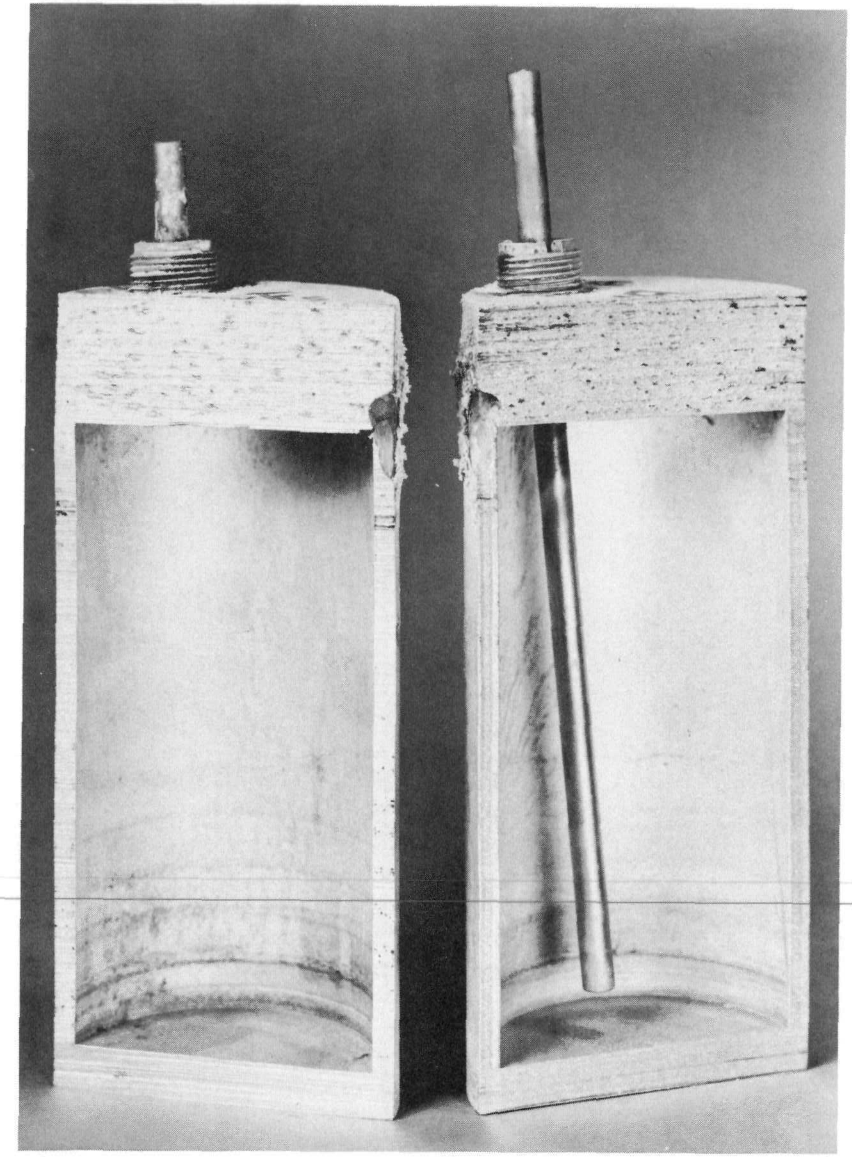

FIGURE 4

By incorporating a condensate receiver into a loop designed to test valve operations, coupons could be maintained in the bromine trifluoride condensate. The condensate was reheated to ~70° C and it overflowed from the coupon container through the test valves back into the still pot.

The data in Table 2 show accelerations of attack from 4 to 20 times those in static long term tests. However, the rates are still satisfactorily low for any use.

Table 2

CORROSION IN BROMINE TRIFLUORIDE CONDENSATE
AT 70° C FOR 650 HR

1 3/8 in. x 1 3/8 in. x 1/16 in. coupons initially polished with fine steel wool and scouring cleanser paste, washed, degreased, and dried at 110° C. Supported in interhalogen condensate between Teflon spacers. Fluoride films were removed with 0.1 M $Al(NO_3)_3$, 0.05 M sulfamic acid, pH 0.5 solution before weighing.

	mil/yr
Nickel	0.036
Welded Nickel	.024
Monel	.10
Welded Monel	.11
K Monel	.19
Inconel	.08

III. CORROSION OF SILVER SOLDER

Early in the laboratory studies with bromine trifluoride solutions, precipitates of silver halides were observed when samples were hydrolyzed in aqueous solutions. Since the total elimination of silver-soldered connections from laboratory equipment was impractical, especially in the Hoke Model 413 diaphragm valve assemblies, a corrosion study of available silver solders was undertaken. Certain limits were placed on the choice of silver solders to be tested. Silver solders containing phosphorus were excluded because of the formation of brittle phosphides with nickel at the brazing temperature with subsequent danger of cracking.[3] Since a hand torch was used in the laboratory on varied sizes of equipment, the choice of low to medium temperature alloys was made. An additional factor was the availability.

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[3] Brazing and Soldering Nickel and High-Nickel Alloys, International Nickel Co., New York, N. Y., Tech. Bul. T-34.

A series of elimination tests were made first by placing 1/4-inch lengths of 1/16-inch diameter solder and 1/4 x 1/4-inch Monel-solder couples in 1/2-inch Fluorothene sample tubes containing bromine trifluoride. These were maintained at 70° C in an oven for 24 hours. Most of the pieces of solder disintegrated (note Figure 6, No. 6). The data presented in Table 3 and Figure 5 were obtained from the couples that remained sufficiently intact to weigh. No attempt was made to remove corrosion products from the samples.

Table 3

CORROSION OF VARIOUS SILVER SOLDERS
IN BROMINE TRIFLUORIDE AT 70 C

1/4-inch Monel squares with silver solder on one side.
Exposed to BrF_3 at 70 C, dried and weighed.

	Silver Solder Composition Weight Per cent					Time of Exposure, hr	Total Penetration, mil/hr
Handy and Harmon	Ag	Cu	Zn	Cd	Other		
Easyflo No. 3	50	15.5	15.5	16	3 Ni	24	0.085
Easyflo No. 45	45	15	16	24		24	0.075
Easyflo No. 35	35	26	21	18		24	.099
RT	60	25	15	-		24	Disintegrated
RTSN	60	30	-	-	10 Sn	24	.15
Easyflo Brazing Alloy	50	15.5	16.5	18		19 1/2	.095
						43 1/2	.065
						115	.037
American Platinum Works							
Silvaloy 35	35	26	21	18		24	0.077
Silvaloy 40	40	18	15	27		24	.086
Silvaloy 45	45	15	16	24		24	.29 (Flaked)
Silvaloy 50	50	15.5	16.5	18		24	.082
Silvaloy 503	50	15.5	15.5	16	3 Ni	24	.12
Silvaloy 355	56	22	17	-	5 Sn	19 1/2	.010
						43 1/2	.0056
						115	.0019
						139	.0016

Additional tests of Silvaloy 355 (American Platinum Works) were conducted in the boiler illustrated in Figure 7 for longer periods of time. The data for liquid, interface and vapor corrosion are presented in Figure 8.

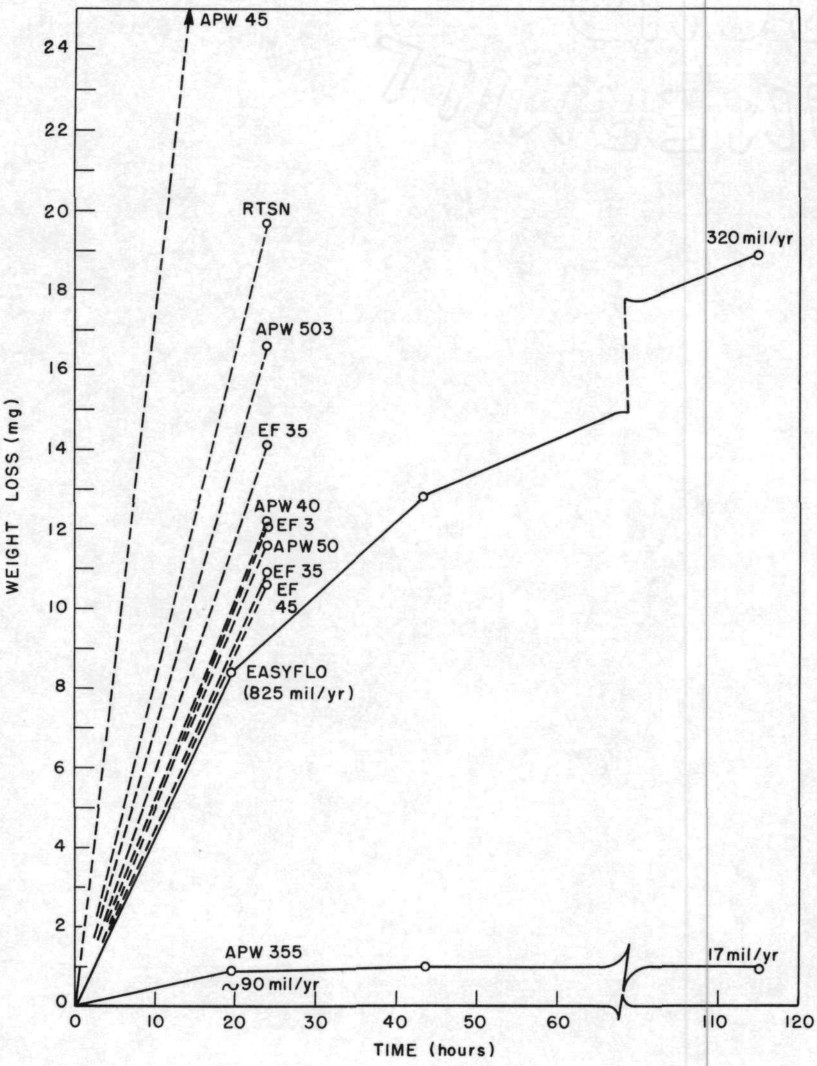


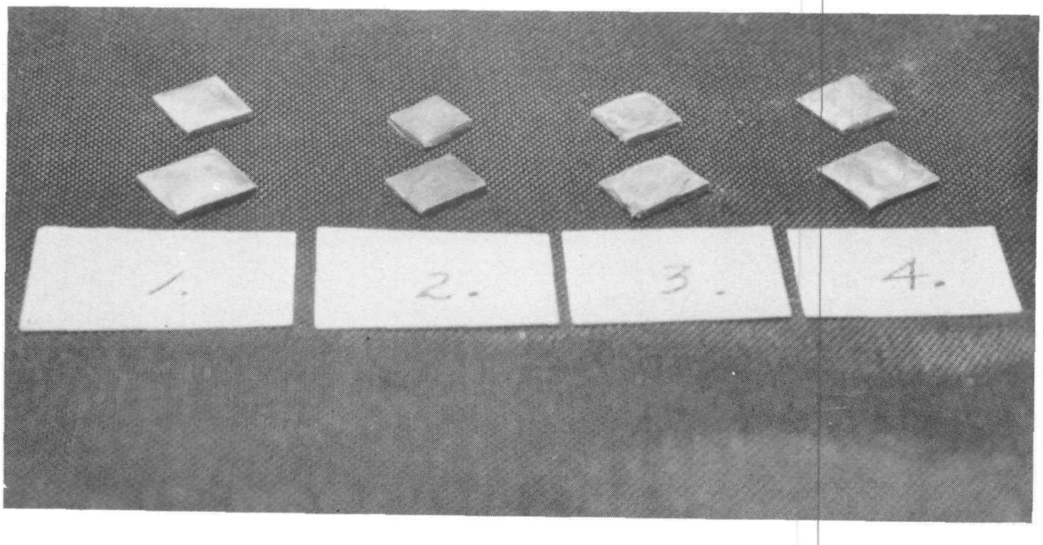
FIGURE 5

CORROSION OF VARIOUS SILVER SOLDER - MONEL COUPLES
IN BROMINE TRIFLUORIDE AT 70°C

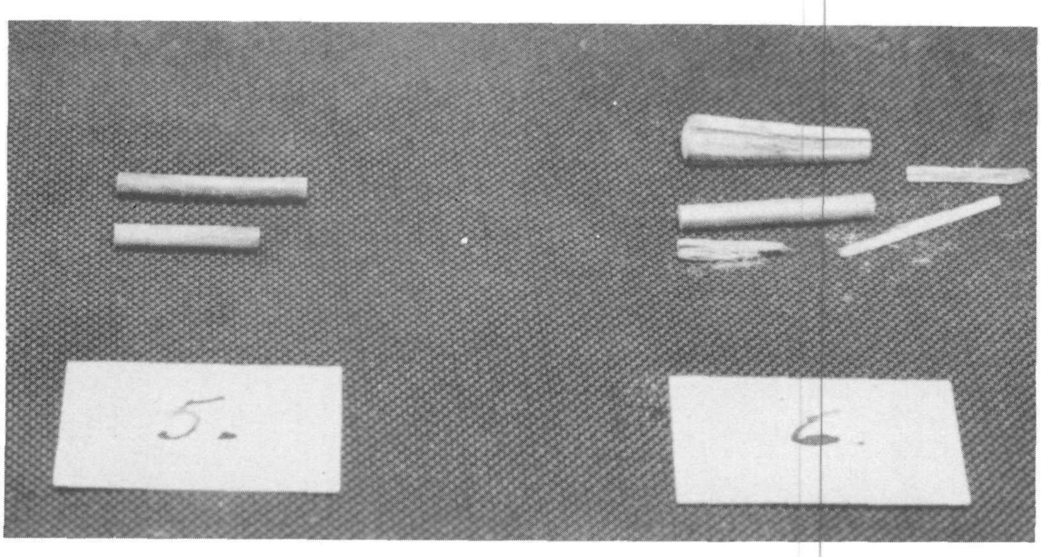
1/4" square of 1/32" Monel with silver solder on one side

There is no clearly defined reason for the superior corrosion resistance of Silvaloy 355 in bromine trifluoride. Comparison with RT and RTSN indicates that neither the absence of cadmium nor the presence of tin seems to be the important factor.

Monel coupons coated on one side with Silvaloy 355 showed a high initial corrosion rate but the rate quickly diminished to less than 12 mils per year based on a three-week's test in bromine trifluoride at 125° C.



A. Samples prepared by coating one side of a Monel coupon with the silver solder being tested.
1. A.P.W. No. 355 couple; original sample.
2. A.P.W. No. 355 couple exposed to BrF_3 six days at 70°C.
3. Easyflo Brazing Alloy couple exposed to BrF_3 five days at 70°C.
4. Easyflo Brazing Alloy couple; original sample.



B. Samples consisted of 1/16-inch wire; an unexposed sample is shown for comparison.

5. A.P.W. No. 355 exposed to BrF_3 six days at 70°C.
6. Easyflo Brazing Alloy exposed to BrF_3 twenty-four hours at 70°C.

FIGURE 6

CORROSION OF SILVER SOLDERS BY BROMINE TRIFLUORIDE

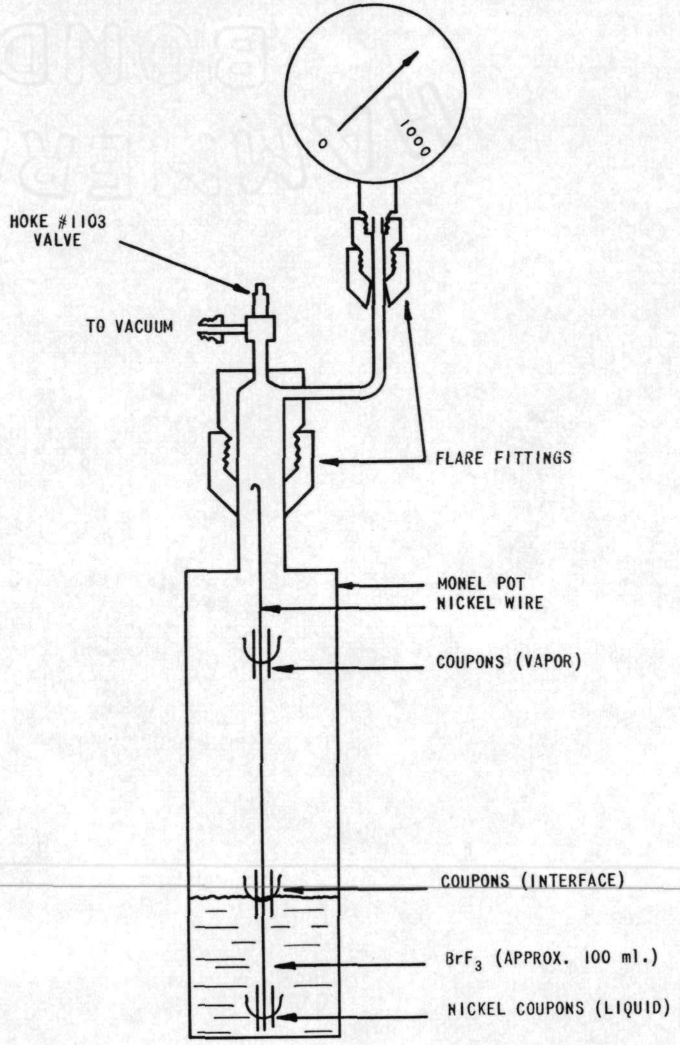

0
1000
HOKE #1103 VALVE
TO VACUUM
FLARE FITTINGS
MONEL POT
NICKEL WIRE
COUPONS (VAPOR)
COUPONS (INTERFACE)
BrF_3 (APPROX. 100 ml.)
NICKEL COUPONS (LIQUID)

FIGURE 7

BOILER FOR CORROSION TESTS WITH BROMINE TRIFLUORIDE

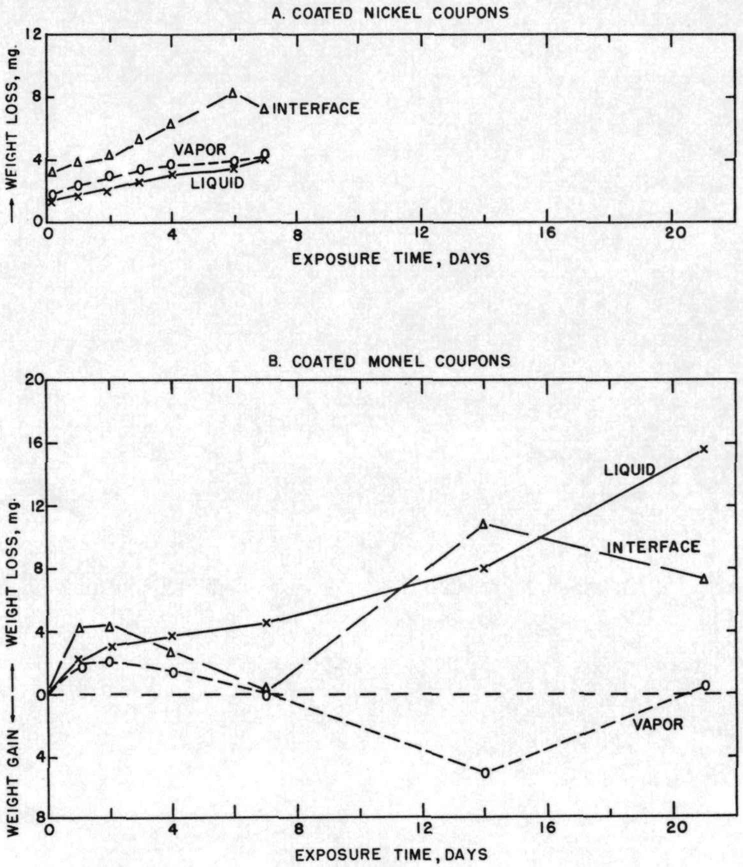


FIGURE 8

CORROSION OF SILVER SOLDER ON NICKEL AND MONEL BY BROMINE TRIFLUORIDE

Type of Silver Solder: American Platinum Works No. 355 (coupons coated on one side only)
Temperature: 125 - 130°C

Coupon Size	Penetration Corresponding to 1 mg. Wt. Loss, mils
In vapor and liquid: 1/2 x 1/2 x 1/32"	0.043
At interface: 1/4 x 1/4 x 1/32"	0.035

15

IV. AQUEOUS CORROSION OF MONEL

A. Aluminum Nitrate Solution Corrosion

During the course of any interhalogen process with radioactive materials it may be essential to decontaminate equipment and subsequently treat and perhaps recover fissionable materials. One acceptable solution for this is aluminum nitrate because of its ability to solubilize fluoride salts through complex formation. Thus, the corrosion rate of Monel in aluminum nitrate solutions is of interest.

The technique adopted for these experiments was in accordance with standard corrosion testing practices. Coupons of Monel were supported on edge on plastic (methacrylate) holders in aluminum nitrate solutions. Preliminary tests showed that various methods of cleaning the coupons, i.e., rinsing with water, scrubbing with soap and water, polishing with a wire brush or crocus cloth, had a negligible effect upon the weight of the coupon or its corrosion rate. Although a thin black film was formed on the surface during the tests, it possessed no measurable weight and appeared to have no inhibiting effects on the corrosion rate.

In order to establish a suitable period of immersion, the effect of time upon the corrosion rate was determined. The samples (1 x 2 x 0.05-inch coupons) were placed in 0.10 M aluminum nitrate solution of pH 3.62 at 26°C. The coupons were then removed after 24, 48, 72, 144 and 312 hours and weighed. The coupon removed after 24 hours was immersed another 24 hours and compared with one immersed for 48 hours, and so forth. This procedure allowed a comparison between the incremental and the total undisturbed corrosion. The results, shown in Figure 9, indicate a constant rate of corrosion over the time period tested. The results are plotted directly as weight loss against time since the coupons were all of the same area. The total time tests showed the same rate, 6 mils/yr, as the increment tests. Since the corrosion rate was found to be independent of time within the interval investigated, an arbitrary standard period of 144 hours was chosen for further runs. This period of time gave a convenient measurable weight loss under these conditions. Later experiments indicated that solutions at lower pH values showed a considerable influence of time on the corrosion rate. Therefore, these data can only correctly be used for intercomparison for the reproduced period of time of 144 hours for low pH values.

Further experiments at 26°C were performed with 0.05 to 0.5 M aluminum nitrate solutions in the pH range of 0.3 to 3.8. The pH values were determined before and after each experiment. All tests were made on duplicate samples for 144 hours. The results, represented in Figure 10, are plotted as corrosion rate versus the average of the initial and final pH. It is apparent that the rate at 26°C was only slightly dependent upon pH, increasing somewhat in the strongly acidic solutions. Variations in the concentration of aluminum nitrate, except as it affected the pH, had no appreciable effect.

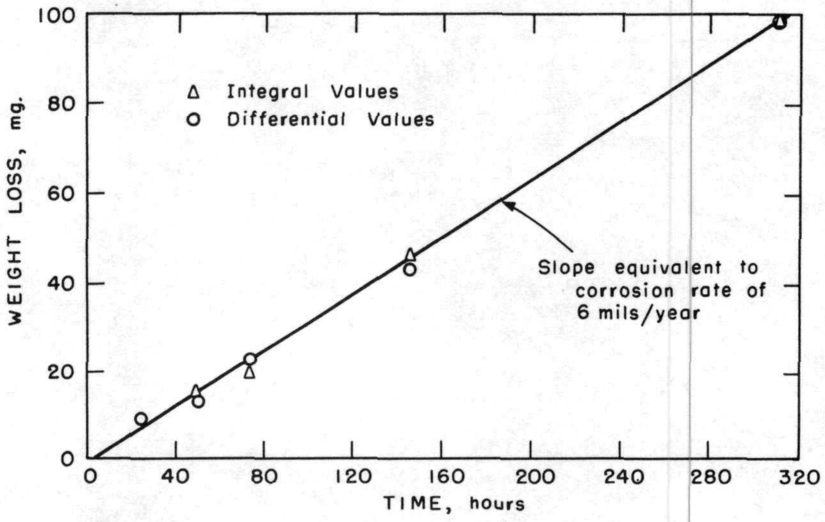


FIGURE 9

EFFECT OF TIME ON THE CORROSION OF MONEL BY ALUMINUM NITRATE

Test Conditions: 0.10 M $Al(NO_3)_3$, pH 3.62, 26°C
Test Specimen: Monel sheet, 1 x 2 x 0.05 in.

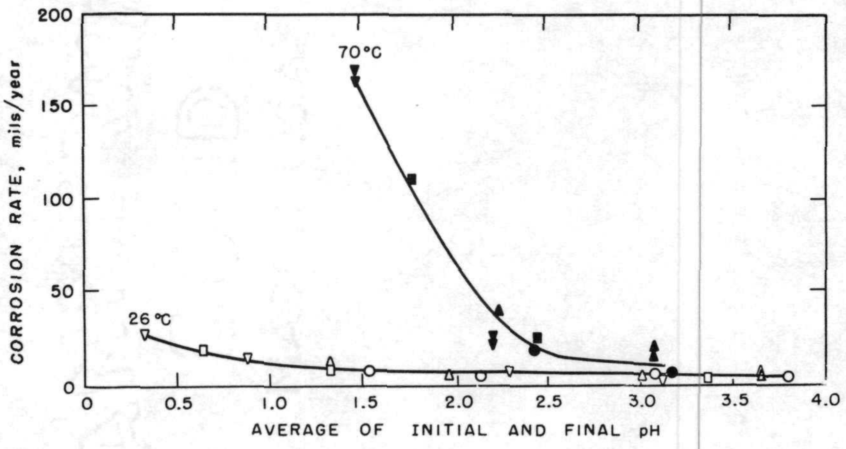


FIGURE 10

EFFECT OF pH ON RATE OF CORROSION OF MONEL IN ALUMINUM NITRATE SOLUTION

Test Specimen: Monel sheet, 1 x 1 x 0.05 in.

KEY:

Aluminum Nitrate Concentration, M	Test Temperature 26°C	Test Temperature 70°C
0.05	○	●
0.10	△	▲
0.30	□	■
0.50	▽	▼

Since faster decontamination of any vessel by operating at higher temperatures might be desirable, corrosion rates at 70°C were investigated briefly. As in the 26°C experiments, the pH was adjusted with nitric acid and the coupons were immersed for a period of 144 hours. The beakers were sealed with sheets of plastic to minimize evaporation and placed in an oven thermostated at 70°C. No definite control of aeration was applied. The corrosion rates at this higher temperature were greater and also much more dependent upon pH. These results are also presented in Figure 10.

The results of these tests suggest that the corrosion of Monel by aluminum nitrate solution is caused by the nitric acid formed as a hydrolysis product. The corrosion rates are less than 30 mil/yr at room temperature, but are generally higher and much more dependent on pH at elevated temperatures for this arbitrary time of 144 hours contact.

B. Sulfamic Acid Inhibition of Nitrate Corrosion

It is believed that nitrous acid is an intermediate species in the corrosion mechanism since the corrosion is probably due to nitrate oxidation of the metal. This hypothesis offers the possibility of inhibiting the corrosion by nitrous acid removal through additions of sulfamic acid, ferrous sulfamate, ferrous sulfate, urea or other similar reagents. Quantitative tests showed sulfamic acid to be the most effective additive. A study of the effectiveness of sulfamic acid and the influence of pertinent variables is presented below.

Most of the tests were of short duration since it is not expected that a particular aluminum nitrate solution would be in contact with Monel for an extended period. The test solutions were de-aerated by bubbling nitrogen through them. All the tests were carried out in a nitrogen atmosphere. Evaporation was minimized by saturating the nitrogen with water vapor before passing it over the test solutions. Runs at 70°C were made in an oven equipped with a vacuum chamber which was flushed with nitrogen and sealed from the atmosphere. Other beakers containing water were placed in the chamber to limit evaporation from the test solutions.

Two Monel coupons, each 1 x 1 x 1/32 inch, were used in each test. These were cleaned in preparation for exposure by one of the following two methods: (1) the coupon was scoured with fine steel wool and a household scouring cleanser, followed by water and acetone rinses; or (2) the coupon was immersed 5 minutes in bromine trifluoride at room temperature, then dipped into 0.5 M aluminum nitrate, hydrazine sulfate solution, rinsed with water and finally acetone. The hydrazine was present to reduce the bromine formed to bromide.

About 125 ml of solution was used for each pair of coupons. All the data reported are average observations for two coupons. Adjustments of acidity were made with nitric acid. Before weighing, each coupon was washed with water and dried with acetone. A weight loss of 1 mg was equivalent to a penetration of 0.003 mil.

Data on the corrosion of Monel by aluminum nitrate solutions at 70° C are given in Table 4 for both scoured and bromine trifluoride-washed coupons with 0 to 0.05 M sulfamic acid concentrations. Data selected from Table 4 are plotted in Figure 11 to illustrate the effect of time and sulfamic acid concentration. The upper curve shows the total corrosion at a particular time by an aluminum nitrate solution in the absence of sulfamic acid. It is of interest that the corrosion is radically reduced after a penetration of 1 mil during the first 150 hours. The reason for this is that as the corrosion proceeds the solution becomes less acid.

Table 4

CORROSION OF MONEL BY ALUMINUM NITRATE SOLUTIONS AT 70 C

Effects of Time, Pretreatment, and Sulfamic Acid Concentrations

Solution: 125 ml of 0.1 M $Al(NO_3)_3$ initially at pH 0.5 with NH_2HSO_3 as indicated.

Coupon Treatment: 1 x 1 x 1/32-in. Monel coupons cleaned before experiment as follows: (1) immersed for 5 minutes in BrF_3 at 25 C, dipped in 0.5 M $Al(NO_3)_3$ saturated with hydrazine sulfate, rinsed in water and dried with acetone - indicated as "BrF_3," or (2) scoured with fine steel wool and scouring cleanser, water washed and dried with acetone - indicated as "Sc."

	Corrosion in Total Mils Penetration												
Sulfamic Acid Concn., M	0	0	0.0005	0.001	0.001	0.002	0.002	0.005	0.01	0.01	0.02	0.05	0.05
Coupon Pretreatment	Sc	BrF_3	BrF_3	Sc	BrF_3	BrF_3	BrF_3	BrF_3	Sc	BrF_3	BrF_3	Sc	BrF_3
Time, Hours													
24	1.1	0.081	0.015	0.25	0.010	0.009	0.009	0.007	0.49	0.006	0.005	0.29	0.006
40	1.6	-	0.15	0.54	0.10	-	0.027	-	0.60	-	-	0.42	-
48	-	0.26	-	-	-	0.012	-	0.011	-	0.010	0.008	-	0.009
64	2.2	-	0.52	0.88	0.46	-	0.28	-	0.77	-	-	0.52	-
71	-	0.52	-	-	-	0.016	-	0.016	-	0.015	0.012	-	0.013
136	3.0	-	-	1.5	-	-	-	-	1.8	-	-	0.84	-
143	-	1.05	-	-	-	0.46	-	0.15	-	0.039	0.023	-	0.027
168	-	1.06	-	-	-	0.76	-	0.36	-	0.19	0.085	-	0.033
192	-	1.06	-	-	-	0.93	-	0.60	-	0.47	0.26	-	0.083
216	-	1.08	-	-	-	1.00	-	0.78	-	0.73	0.84	-	0.23

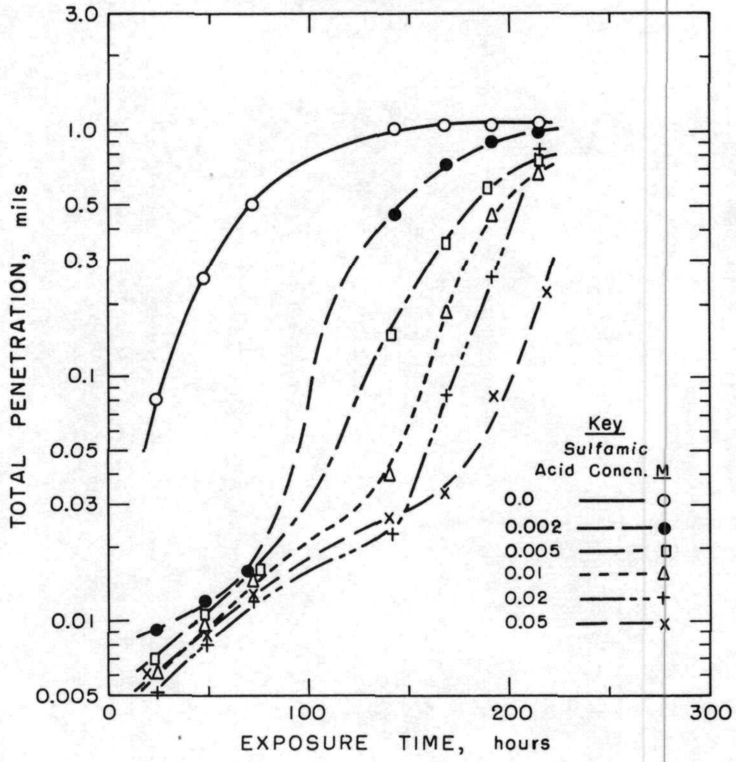


FIGURE 11

INHIBITING NITRATE CORROSION OF MONEL WITH SULFAMIC ACID

Temperature: 70°C
Test Coupons: 2 - 1 x 1 x 1/32" Monel, washed with BrF_3
Corrodent: 125 ml. 0.1 M Aluminum Nitrate, pH = 0.5 (initially) with Sulfamic Acid as indicated
Atmosphere: Nitrogen

The previously mentioned study demonstrated that the corrosion of Monel by aluminum nitrate is primarily dependent on the solution acidity and not the aluminum nitrate concentration. Under the conditions of these experiments it was found that for sulfamic acid concentrations of 0 to 0.05 M at 70° C, the acidities of the solutions all decreased, corresponding to a pH increase from 0.5 to 4 in 168 hours. The data presented in Figure 10 show that at 70° C and a pH of greater than 2.5, the corrosion is small and constant, while in more acid solutions the corrosion is much greater. It is, therefore, important to emphasize that in this type of corrosion the total penetration is a function of the ratio of metal area to the solution volume, and that the pH of the solution is controlled only at the beginning of the exposure.

The corrosion inhibition is shown to increase with increasing sulfamic acid concentration in Figure 11. The inhibiting effect is appreciable for 75 hours at a sulfamic acid concentration of 0.005 M. This effect decreases the corrosion by a factor of about 30. For 0.01 M sulfamic acid the effect lasts for about 140 hours, for 0.02 M about 150 hours and for 0.05 M about 165 hours. From these data it is apparent that it is not particularly worthwhile for washing vessels to use sulfamic acid concentration greater than 0.01 M.

The magnitude of these effects is also a function of the coupon pretreatment. In Figure 12 the effect of coupon pretreatment on the corrosion of Monel by aluminum nitrate in the presence and absence of sulfamic acid is demonstrated. It is obvious that the coupons immersed in bromine trifluoride, followed by aqueous washes, are considerably more corrosion resistant than those cleaned mechanically. In the absence of sulfamic acid, this improvement is a factor of 3 to 10. In the presence of the corrosion inhibitor, the improvement is from fifty to eighty fold. It is hard to understand the rather profound effect of this bromine trifluoride dip pretreatment, but fortunately the bromine trifluoride contact is similar to the expected mode of operation as related to the vessel to be decontaminated.

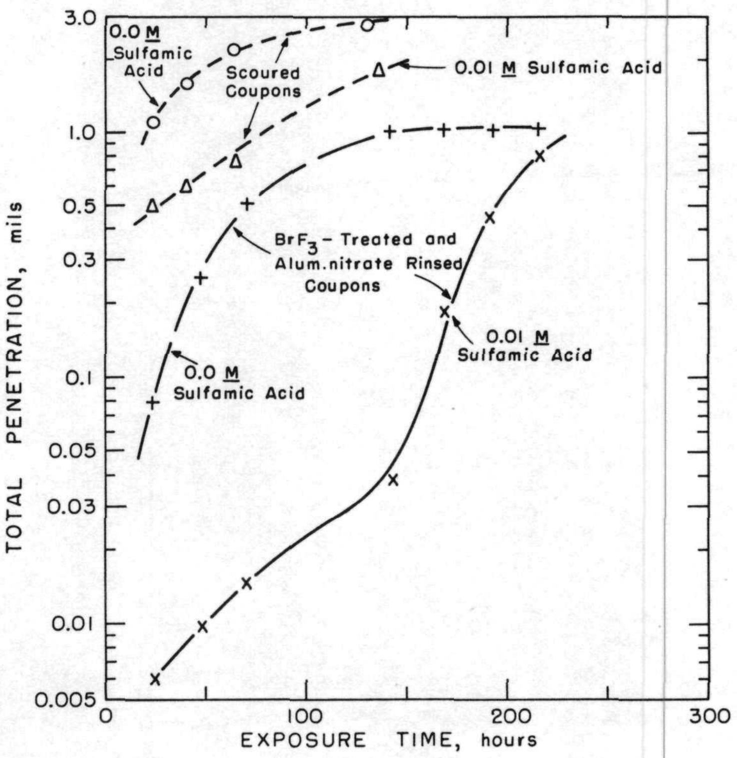


FIGURE 12

EFFECT OF COUPON PRETREATMENT ON NITRATE CORROSION OF MONEL

Temperature: 70°C

Test Coupons: 2- 1 x 1 x 1/32" Monel

Corrodent: 125 ml. 0.1 M Aluminum Nitrate, initial pH = 0.5 with Sulfamic Acid as indicated

Atmosphere: Nitrogen

In Table 5 data are shown for room temperature corrosion of Monel by 0.1 M aluminum nitrate. Corrosion is considerably less than at 70° C. In Figure 13 are presented the corrosion data at two temperatures with and without sulfamic acid. In the absence of sulfamic acid, it can be seen that the corrosion is increased by a factor of perhaps 60 by increasing the temperature 45 degrees. However, in the presence of 0.01 M sulfamic acid at the end of 50 hours the corrosion is increased by a factor of only 4 for the same temperature increase. These data also point out that sulfamic acid does not so dramatically inhibit the already low corrosion at room temperature as it does at the elevated temperatures. Thus, it may be concluded that the inclusion of sulfamic acid in the wash solution would be most useful if it were necessary to heat the solution, or if the possibility of the solution becoming warm could not be avoided.

Table 5

CORROSION OF MONEL BY ALUMINUM NITRATE SOLUTIONS AT ROOM TEMPERATURE

Temperature: 20 to 30 C.

Solution: 125 ml of 0.1 M $Al(NO_3)_3$ at pH 0.5 with sulfamic acid as indicated.

Coupon Treatment: 1 x 1 x 1/32-in. Monel coupons cleaned before weighing as follows: (1) immersed for 5 minutes in BrF_3 at 25 C, dipped in 0.5 M $Al(NO_3)_3$ saturated with hydrazine, rinsed in water and dried with acetone - indicated as "BrF_3," or (2) scoured with fine steel wool and scouring cleanser, water washed and dried with acetone - indicated as "Sc."

	Corrosion in Total Mils Penetration									
Sulfamic Acid Concn., M	0	0	0.001	0.002	0.005	0.01	0.01	0.02	0.05	0.05
Coupon Treatment	Sc	BrF_3	Sc	BrF_3	BrF_3	Sc	BrF_3	BrF_3	Sc	BrF_3
Time, Hours										
24	0.082	-	0.042	-	-	0.048	-	-	0.026	-
48	-	0.004	-	0.003	0.003	-	0.003	0.004	-	0.004
96	0.156	-	0.047	-	-	0.078	-	-	0.046	-
144	-	0.006	-	0.004	0.003	-	0.003	0.004	-	0.004
192	-	0.007	-	0.004	0.004	-	0.004	0.005	-	0.005
288	-	0.010	-	0.005	0.005	-	0.006	0.006	-	0.006

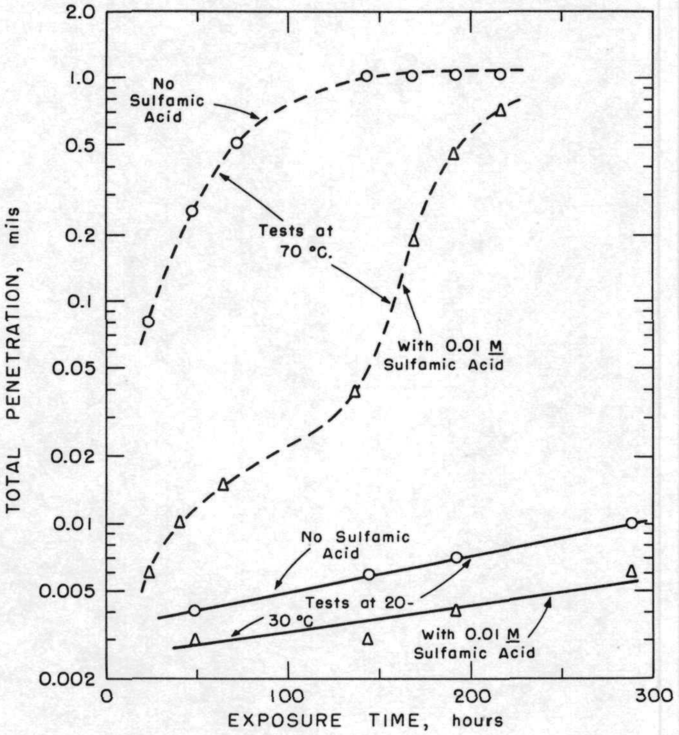


FIGURE 13

EFFECT OF TEMPERATURE ON NITRATE CORROSION OF MONEL

Test Coupons: 2 - 1 x 1 x 1/32" Monel, washed with BrF_3
Corrodent: 125 ml. 0.1 M Aluminum Nitrate, initial pH = 0.5, with Sulfamic Acid as indicated
Atmosphere: Nitrogen

The effect of the initial pH of the solution has been briefly reexamined. The data presented in Table 6 show that as the pH is increased, the corrosion rates decrease. For example, at a pH of 0.2, the corrosion of the scoured coupons at 70° C is 0.63 mil in 24 hours, while at a pH of 1.5 the rate is about one-tenth this value. At 25° C the change is less marked, since the rates at low pH are already quite low.

These data have pointed out that after an interval of time dependent on the initial sulfamic acid concentration the inhibition effect is lost. This is shown by the plots on Figure 11. It was of interest to know whether the sulfamic acid would still be able to inhibit corrosion if the wash solutions were kept in the absence of Monel during the period of inhibition. An experiment was performed to attempt to answer the question of whether the sulfamic acid is destroyed by nitrous acid formed by ordinary nitrate decomposition or whether it is destroyed by nitrous acid produced during the Monel-nitrate reaction. The progress of corrosion with a freshly prepared aluminum nitrate solution at 70° C was compared with that of a solution aged 144 hours at 70°C in the absence of Monel. The data obtained are plotted in Figure 14. It can be seen that the inhibition effect is lost if the solution is stored in the absence of Monel. The total penetration is only a little less for solutions kept in the absence of Monel during the inhibition period than for those in the presence of Monel during the entire aging period.

Table 6

EFFECT OF pH ON NITRATE CORROSION OF MONEL

Solution: 125 ml of 0.1 M $Al(NO_3)_3$, 0.05 M NH_2HSO_3

Coupon Treatment: 1 x 1 x 1/32-in. Monel coupons cleaned before test as follows: (1) immersed for 5 minutes in BrF_3 at 25°C, dipped in 0.5 M $Al(NO_3)_3$ saturated with $N_2H_4 \cdot H_2SO_4$, rinsed in water and dried with acetone - indicated as "BrF_3"; or (2) scoured with fine steel wool and scouring cleanser, water washed and dried with acetone - indicated as "Sc."

Initial Solution pH	Coupon Pretreatment	Test Duration, hours	Total Penetration, mils at 25°C	Total Penetration, mils at 70°C
0.2	Sc	24	0.05	0.630
0.5	Sc	24	0.03	0.290
1.5	Sc	24	0.01	0.058
0.2	BrF_3	48	0.009	0.152
0.5	BrF_3	48	0.004	0.009
1.5	BrF_3	48	0.006	0.012
3.0	BrF_3	48	0.003	0.016

In summarizing it can be said that:

(1) Sulfamic acid will inhibit the corrosion of Monel by 0.1 M aluminum nitrate at a pH of 0.5 for a period of time dependent upon the sulfamic acid concentration.

(2) A sulfamic acid concentration of 0.01 M appears to assure corrosion inhibition at 70° C for a 0.1 M aluminum nitrate solution at a pH of 0.5 for more than 100 hours.

(3) A sulfamic acid concentration greater than 0.01 M is probably not practical since the subsequent extension of the inhibition is small.

(4) The sulfamic acid-aluminum nitrate wash solutions should be used immediately after preparation since the effect of the sulfamic acid is lost on standing.

(5) If there is assurance that the solution temperature will not rise appreciably above 25°C, the advantage gained by using sulfamic acid is small.

(6) The combination of sulfamic acid in the aluminum nitrate solution and the pretreatment with bromine trifluoride showed a greater inhibition.

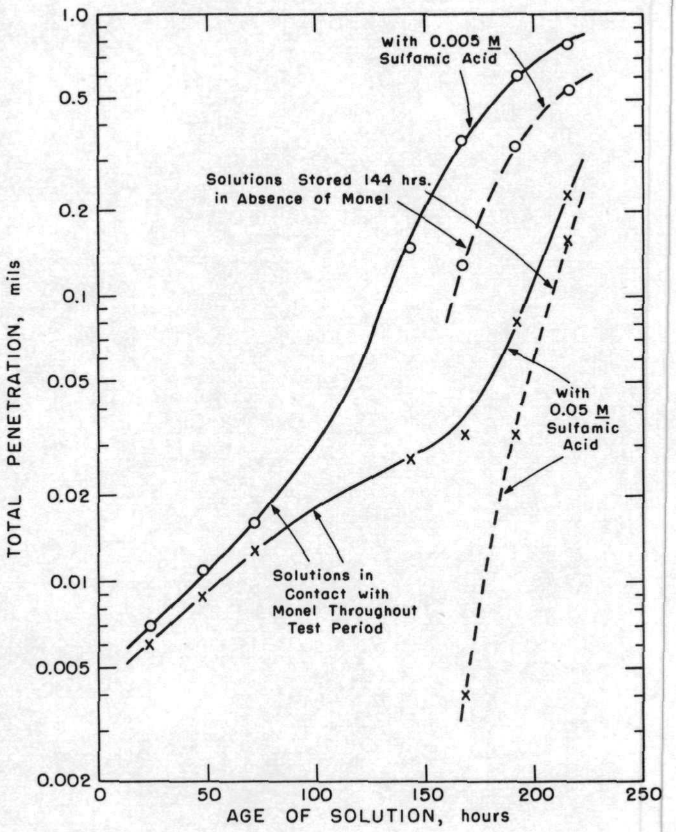


FIGURE 14

EFFECT OF SOLUTION AGE ON INHIBITING NITRATE CORROSION OF MONEL WITH SULFAMIC ACID

Temperature: 70°C
Test Coupons: 2- 1 x 1 x 1/32" Monel, washed with BrF_3
Corrodent: 125 ml. 0.1 M Aluminum Nitrate, initial pH = 0.5

V. CORROSION OF MONEL EXPOSED ALTERNATELY TO BROMINE TRIFLUORIDE AND CERTAIN AQUEOUS SOLUTIONS

To decontaminate satisfactorily any vessel used in a bromine trifluoride process involving radioactive materials, the Monel will necessarily be alternately exposed to bromine trifluoride and various aqueous washes. Aluminum nitrate solution is the most practical decontamination agent. The additional steps itemized below were intended to simulate the treatment of a Monel dissolver for processing uranium fuel rods. Step 9 employs a typical decanning solution such as would be used initially in a process to remove the aluminum cans from uranium rods prior to bromine trifluoride treatment.

The coupons prior to treatment were cleaned in the same procedure described in Section I for the long term corrosion tests, i.e., polished with a paste of water and scouring cleanser supported on fine steel wool. They were supported between Teflon spacers in the rack and exposed in the following steps:

(1) Placed in boiler (illustrated in Figure 15).

(2) Fluorinated at 1000 mm pressure with chlorine trifluoride at room temperature for 10 minutes.

(3) Boiler evacuated.

(4) Treated with liquid bromine trifluoride at 125°C and maintained under reflux for 20 hours.

(5) Liquid removed, boiler evacuated while maintaining heat.

(6) Allowed to cool, helium admitted, and coupon rack removed from boiler.

(7) Coupons treated with one liter 1 $\underline{M}$ aluminum nitrate, 0.05 $\underline{M}$ sulfamic acid, pH 0.5 at room temperature for 4 hours.

(8) Rinsed with distilled water for 10 minutes.

(9) Coupons treated with one liter 2.8 $\underline{M}$ sodium hydroxide, 2.7 $\underline{M}$ sodium nitrate solution at approximately 90°C for 4 hours.

(10) Rinsed with distilled water (time varied to suit regular working hours).

(11) Dried at 100°C for 1/2 hour.

26

The coupons were weighed at the completion of the first, second, third, tenth, twelfth and fourteenth cycles. The attack was uniform throughout the test and the corrosion rates given in Table 7 were calculated from the weight losses.

Because the corrosion rates were all less than 0.005 mil per cycle it appears feasible to alternate interhalogen systems and aqueous systems under conditions similar to those set forth in these experiments.

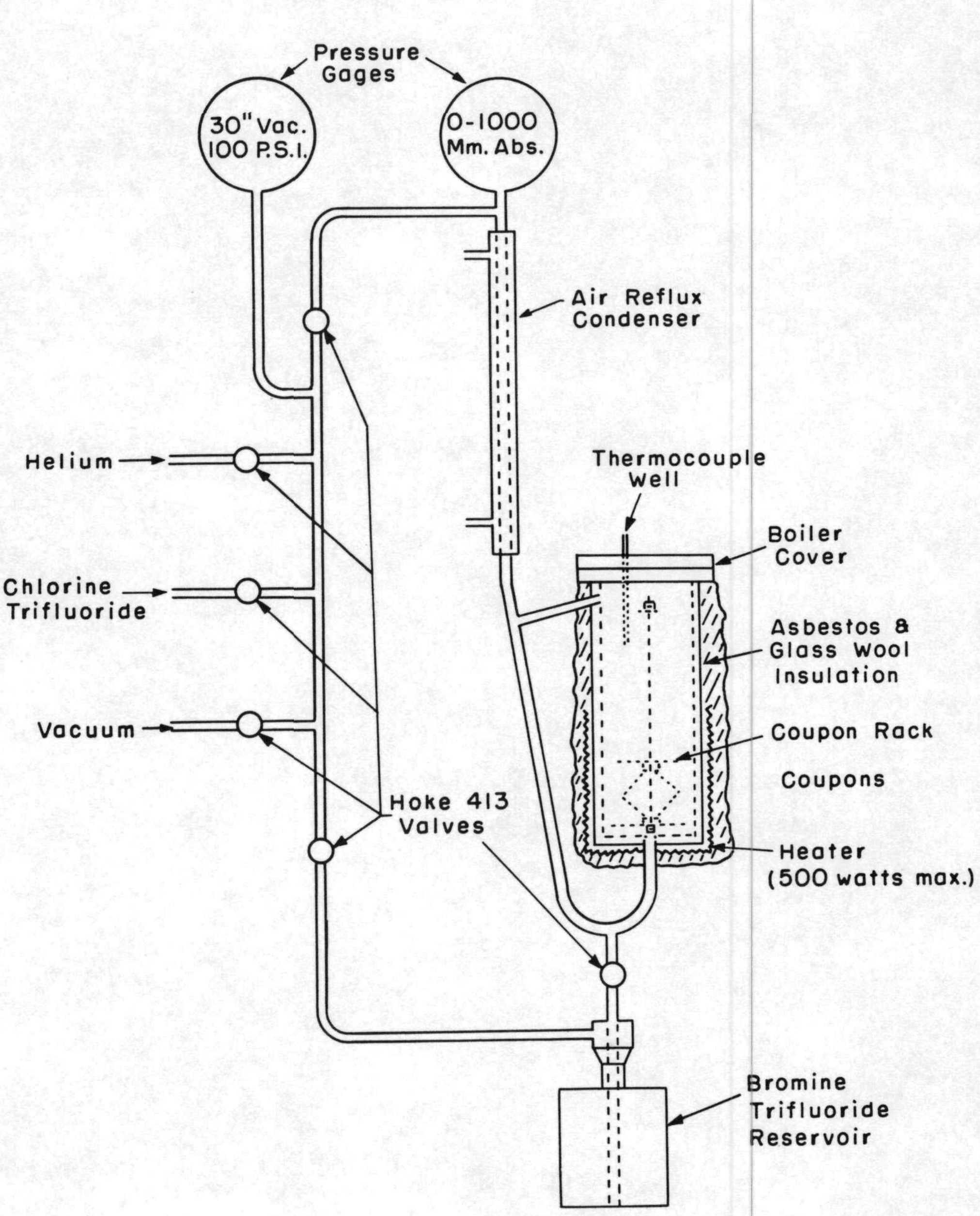

Pressure Gages
30" Vac.
100 P.S.I.
0-1000
Mm. Abs.
Air Reflux Condenser
Helium
Chlorine Trifluoride
Vacuum
Thermocouple Well
Boiler Cover
Asbestos & Glass Wool Insulation
Coupon Rack
Coupons
Hoke 413 Valves
Heater (500 watts max.)
Bromine Trifluoride Reservoir

FIGURE 15

BOILER FOR INTERHALOGEN PHASE OF CYCLIC CORROSION

Table 7

CORROSION RATES OF HIGH NICKEL ALLOYS SUBJECTED TO ALTERNATE INTERHALOGEN - AQUEOUS SYSTEMS

(As given in the text)

Coupons 1 3/8 x 1 3/8 x 1/32 inch polished
with scouring cleanser and fine steel wool.

Metal	Corrosion (mils per cycle)
Nickel	0.0047
Welded Nickel	0.0041
Monel	0.0044
Welded Monel	0.0044
K Monel	0.0047
Inconel	0.0040

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