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CORROSION OF SOME REACTOR MATERIALS IN DILUTE PHOSPHORIC ACID

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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by

J. E. Draley, S. Greenberg, and W. E. Ruther

ABSTRACT

Corrosion tests in dilute phosphoric acid (pH 3.5) at elevated temperature are described for X8001 aluminum, 18-8 stainless steels, aluminized carbon steel, and Zircaloy.

In a 307-day dynamic test at 18 ft/sec and 315°C, X8001 aluminum corroded at a rate of $\frac{1}{2}$ mdd for the first 240 days. In subsequent exposures, the corrosion rate increased, but the total average penetration at 307 days was only 0.0005 inch. At 200 days, the total corrosion in this test was one-fiftieth that in distilled water. Static tests at 225°C gave corrosion rates too low to measure (<0.2 mdd).

Of several different 18-8 stainless steels tested in this solution at 315°C, only sensitized type 316 suffered intergranular attack. General attack rates of the other samples, of the order of $\frac{1}{4}$ mdd, were obtained for the period from 94 to 186 days. Although this is much larger than the rate in distilled water, it represents a penetration rate of only about 5×10^{-5} inch/year.

Aluminized carbon steel did not suffer rapid corrosion in this solution at 315°C, even when large areas of the carbon steel were exposed. There was a tendency for corrosion to separate the steel and aluminum with some specimens, depending on the heat treatment.

Zircaloy-2 and Zircaloy-3 corrosion were of the same order in this solution at 315°C as in water.

INTRODUCTION

Since 1942, aluminum has seemed a logical choice for fuel element cladding in nuclear reactors. Its absorption cross section is low, its cost is low, its technology is reasonably well known, and its corrosion resistance

in water is acceptable at moderate temperatures. However, at temperatures suitable for the production of economic power, the corrosion of commercial alloys is unacceptably rapid.

Since the development of special alloys for this application,[1] the prospect of using aluminum has seemed more likely. Unfortunately, the special alloys have shown corrosion rates strongly dependent upon water composition, especially at high flow rates. Under unfavorable operating conditions (leading to undesirable water composition), corrosion rates have been observed to be unacceptably high.

In an effort to remedy this situation, some effort has been made to inhibit the corrosion of the special alloys, such as X8001. In this group the inhibition studies culminated, in 1956, in the observation that a phosphoric acid solution at pH 3.5 (room temperature) almost completely prevented corrosion of this alloy at 290°C. The results of our experiments showing the effects of phosphate and hydrogen ion concentrations have been reported.[2] Some additional static corrosion tests have been run since, and these are herein described.

The very promising results obtained created an interest in the behavior of this alloy in such solutions at high flow rate. Corrosion in phosphoric acid solutions more dilute than pH 3.5 has been studied by Grant[3] of the ANL Reactor Engineering Division and by General Electric Company personnel at Hanford and Vallecitos. At pH 3.5 a brief test by I. Cohen[4] at 343°C indicated excellent corrosion resistance at a flow rate of 20 feet per second. At Hanford and, on a subcontract to Argonne, at the Babcock and Wilcox Research Center, efforts were made to extend the testing time and hence to provide more valuable results. An apparent sensitivity to weld zone corrosion of stainless steel loop components in this environment restricted the Hanford efforts. At Babcock and Wilcox the results were compromised by mechanical failure of a pump bearing in the middle of the test. This type of test has now been repeated at Argonne, and is included in this report.

With the good behavior of the aluminum alloy indicated, it was of interest to determine the feasibility of using other reactor materials in this environment. The results of corrosion tests having this objective conclude this report.

EXPERIMENTAL

The static corrosion tests were performed in a constantly refreshed stainless steel autoclave system, which has been previously described.[1] The samples were electrically insulated from the stainless steel by artificial sapphire rods.

The dynamic experiments were performed in test loops. A high-pressure circulating pump maintained the flow of liquid past the samples. A small pump continuously fed fresh H_3PO_4 solution of pH 3.5 into the loop. The pressure of the loop was maintained by a Grove back-pressure regulator at several hundred psi above the vapor pressure of the solution. The discharge of the regulator went to the drain. The samples were $\frac{1}{2}$ x 2 x $\frac{1}{8}$ -in. plates with $\frac{3}{32}$ -in. dia semicircular channels milled in the $\frac{1}{8}$ x 2-in. edges. The shape was chosen to fit an existing eddy current thickness gauge[5] and to permit electrical insulation of the samples from the stainless steel by artificial sapphire rods. Details of construction have previously been published[6] for one of the two loops used in this study.

The materials used for samples were X8001 aluminum (0.89 w/o Ni-0.48 w/o Fe-0.13 w/o Cu-0.11 w/o Si), Zircaloy-2, Zircaloy-3, Types 304, 347 and 316 stainless steel, and 1020 carbon steel aluminized with X8001 alloy by the Chicago Metallizing Corporation.

The aluminum was heat treated for 10 days at 315°C prior to dynamic testing to reduce subsequent heat treatment effects on the eddy current gauge. The surface of the samples was prepared by etching in a 50 H_2O : 50 HNO_3 : 10 HF (by volume, using reagent grade acids) mixture and rinsing in distilled water.

The Zircaloys were etched in a similar mixture of acids, immediately transferred to 50 H_2O : 50 HNO_3, and then rinsed in distilled water. Some samples were also tested with surfaces prepared by wet grinding (240 grit Durite).

The stainless steels were tested in both the quench annealed and the sensitized (at 704°C for 24 hours) condition. As with the Zircaloys, both etched and wet ground surfaces were tested.

Samples of the aluminized carbon steel were heat treated in air and in vacuum at 704°C for $\frac{1}{2}$ hour. A longer (2-hour) treatment in vacuum at 732°C was also used. Other specimens were tested in the as-sprayed condition. Some specimens were sectioned to expose various surfaces of carbon steel. No special surface preparation except degreasing was used on the aluminized coating.

Eddy current thickness gauge readings coupled with the destructive defilming of samples by the methanol-iodine method were used to evaluate the corrosion of aluminum X8001 vs time, except as noted in the text. For the other materials, the samples were weighed with their corrosion coating intact and the results obtained as weight change per cm^2 vs time.

The solution was made up using C.P. orthophosphoric acid and doubly distilled water. The refreshment rate was about 10 cc/min for the static systems and about 35 cc/min for the dynamic systems. The pH was measured at room temperature by means of a Model G Beckman pH meter. The effluent from the tests measured within the range pH 3.55 ± 0.06.

DATA AND RESULTS

X8001 Aluminum Alloy

Static: This alloy was corrosion tested in autoclaves at 225°C. Two concentrations of phosphoric acid were used; one at pH 3.5 and one at pH 4.0. The replenishing solution was helium saturated.

Each point in Fig. 1 represents the amount of corrosion which occurred with one sample. The values were determined after removal of the corrosion product by successive treatments in boric acid and in chromic-phosphoric acid solutions, an older defilming technique. The amount of scatter shown is not abnormal; it is a result of unknown film-stripping errors, and the variation in behavior between samples. Because of the scatter it is not possible to estimate corrosion rates closer than about 0.05 mil/yr. No significant slope of the curve (or "corrosion rate") could be estimated at pH 3.5. There is no real assurance that the corrosion curve at pH 4.0 is truly a straight line. It was drawn that way in the absence of more reliable information.
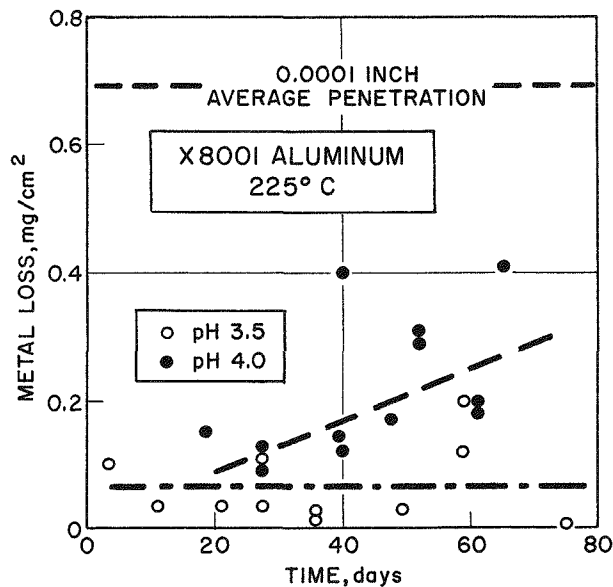

Fig. 1

Corrosion of X8001 Aluminum in Dilute Phosphoric Acid

These samples were examined for pitting at the end of the test. A few very shallow microscopic pits of about 0.06-mm diameter were noted on some samples and were completely absent on others. There was no

correlation between length of time in test and the number or size of the pits. The corrosion rates obtained in these tests are compared in Table I with previously reported rates[2] at a slightly higher temperature.

Table I

STATIC CORROSION OF X8001 ALLOY IN
DILUTE PHOSPHORIC ACID

Temperature (°C)	pH (measured at room temperature)	Approx. Corrosion Rate (mils/year)
225	3.5	<0.05
	4.0	0.2
290	3.5	<0.05
	4.5	1.0

Couples: The effect of electrically coupling samples of X8001 alloy to stainless steel was also investigated in static tests at 225°C to determine the extent of damage that might result from such coupling in a reactor application. Couples were made by passing type 304 stainless steel bolts through an aluminum sample. The behavior of the couples was similar in pH 3.5 and pH 4.0 acid. At the first viewing period, the pH 4.0 samples showed an irregular encrustation of white corrosion product (loosely attached) on the aluminum next to the stainless steel. The corrosion product did not increase with time and most of it had fallen off by the end of the test. The pH 3.5 couples did not show this encrustation initially, but a replacement sample at this pH exhibited it to a somewhat lesser extent.

Under the microscope the 40 and 80-day samples were quite similar in appearance. A lacework of microscopic pits in the aluminum surface near the stainless steel was filled with a white corrosion product. There was no pitting under the washers or bolt heads, and only slight attack on the inside of the bolt holes in the aluminum. There was no sign of an accelerated attack on the stainless steel due to its coupling with the aluminum. When the 80-day samples were defilmed, it was obvious that the lacework of pits extended further from the stainless steel for the pH 4.0 test than for the one at pH 3.5. Also, the total amount of microscopic pitting was greater for pH 4.0 exposure. There had been no serious penetration in either case.

A similar couple test (18-8 stainless steel vs X8001) was performed in helium-saturated, pH 3.5 H_3PO_4 at 315°C. Crevice evaluation samples made by fastening two pieces of aluminum sheet together were also exposed in this test. Four couples and four crevice couples were exposed.

There was no noticeable effect of coupling to stainless steel during the test period of 106 days. One member of an X8001-X8001 crevice sample had a string of very small blisters located in or near the contact area. These were noted at about 16 days, but did not grow during the rest of the test.

Dynamic Test: The dynamic corrosion experiment for X8001 aluminum in pH 3.5 H_3PO_4 clearly indicated the improvement in corrosion resistance in this environment (Fig. 2). The distilled water and pH 5.5 curves were previously reported[2] and are included for comparison. For example, the total corrosion at the end of previous tests was 62 mg/cm^2 for water and 17 mg/cm^2 in pH 5.5 H_3PO_4. At the same exposure time, the corrosion was only 1.1 mg/cm^2 in pH 3.5 H_3PO_4 (7 $mg/cm^2 \approx 10^{-3}$-inch penetration).

Fig. 2
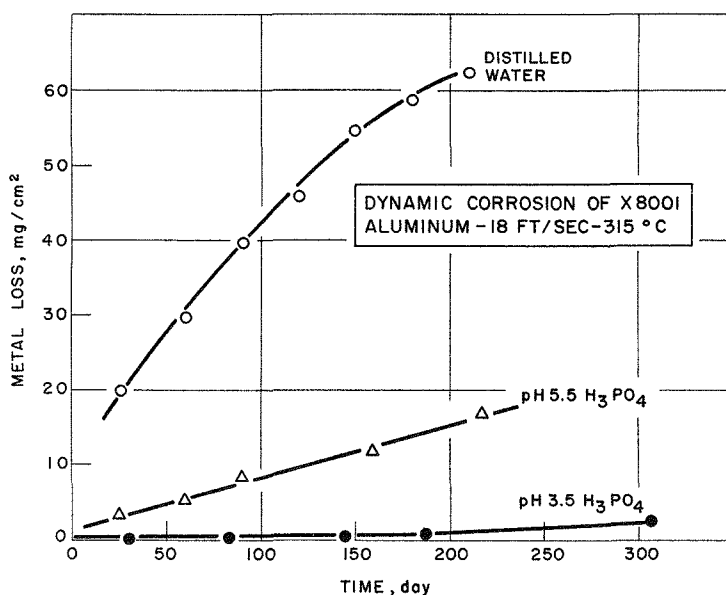
Comparison of the Dynamic Corrosion of X8001 Aluminum at 315°C in Water and Dilute Phosphoric Acid

The corrosion points obtained by defilming the specimens are plotted in Fig. 3 with an expanded scale to show more clearly the two types of corrosion experienced.

Fig. 3

Dynamic Corrosion of X8001 Aluminum in Dilute Phosphoric Acid. (Eddy Current Points are Averaged Data from Four Samples.)
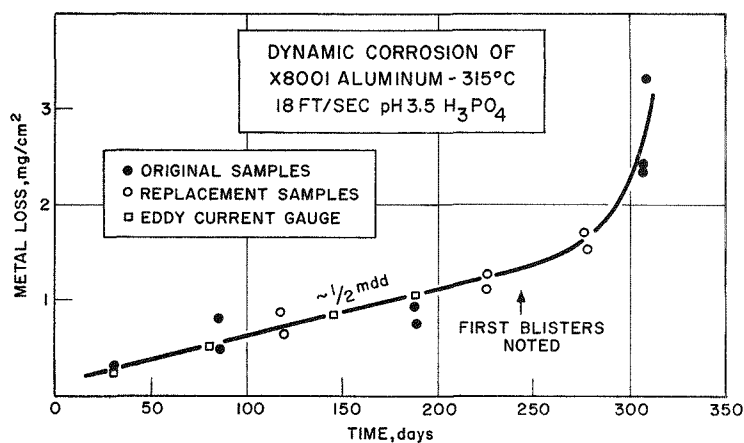
Up to about 240 days the samples were coated with a blue-green smooth corrosion product which darkened with time of exposure to a very dark grey. Figure 4 shows a typical sample in this period.
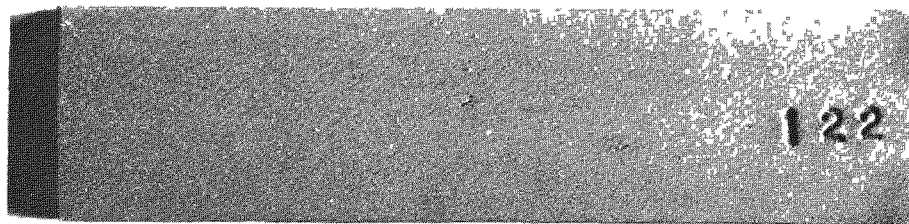
100,599   2.3X

Fig. 4. Appearance of Typical X8001 Sample Exposed
for 119 Days in pH 3.5 H_3PO_4, 18 ft/sec, 315°C.

At about 240 days the previously smooth corrosion coating showed a few tiny blisters. The blistering accelerated throughout the remainder of the test. A sample exposed the full 307 days is shown in Fig. 5.
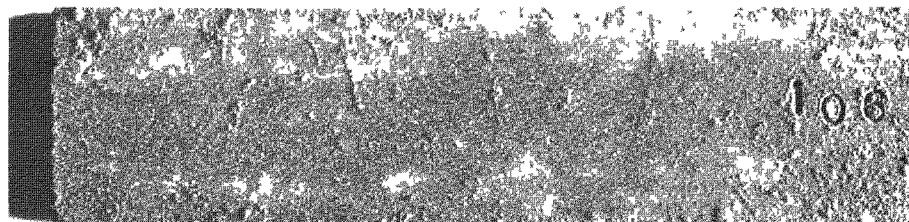
100,601   2.3X

Fig. 5. Appearance of Typical X8001 Sample Exposed
for 307 Days in pH 3.5 H_3PO_4, 18 ft/sec, 315°C.

A micrograph at high magnification (see Fig. 6) of a cross section of a sample exposed 307 days clearly shows the subsurface voids. The corrosion product on the inner surface of the voids indicated that a path existed for the entrance of water. Some smaller, more angular voids without corrosion product linings were noted in the metal further from the corrosion interface. This suggested that corrosion product hydrogen was enlarging the voids initially, followed by water corrosion in those voids for which a water pathway had been opened.

The corrosion curve up to the onset of blistering was linear with a slope of about $\frac{1}{2}$ milligram per decimeter per day (mdd); after blistering, the slope rapidly increased. Changes of rate of this sort have been reported for some long-term tests of some melts of X8001 in water in static autoclaves. This makes it impossible to clearly define the H_3PO_4 as the causative agent in this experiment. It should be pointed out that the close agreement between replacement samples and samples left in the entire test is unusual in the dynamic corrosion of aluminum.
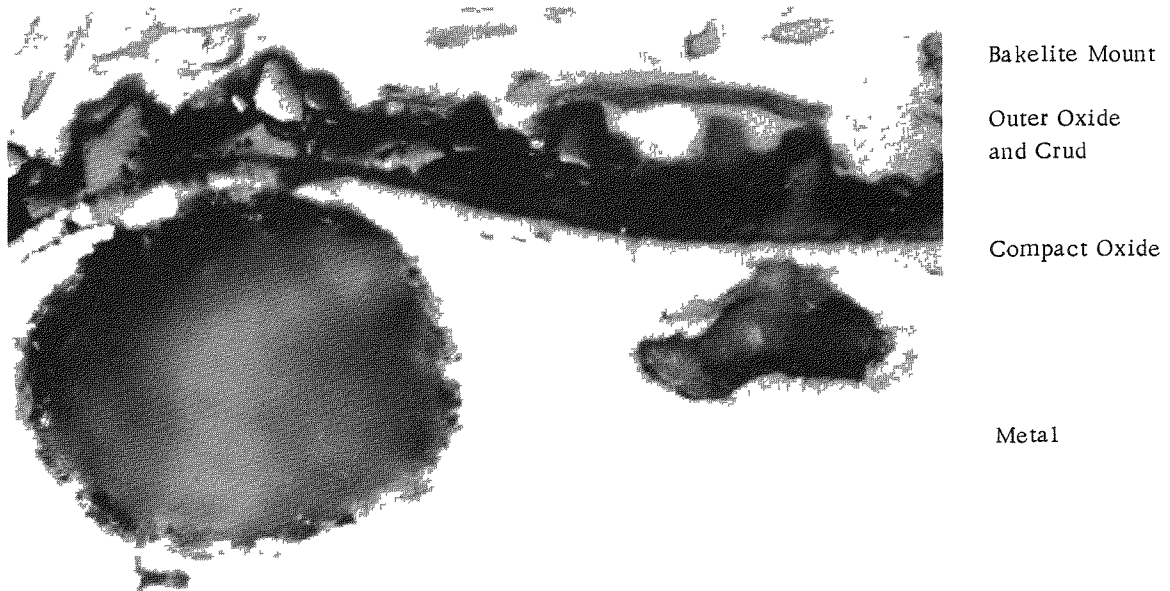
110,296   1000X

Fig. 6. Corrosion Interface of X8001 Sample Exposed
307 Days in pH 3.5 Phosphoric Acid (18 ft/sec).

A portion of the corrosion product from a sample exposed 307 days
was submitted to the X-ray group for identification. The strong pattern
obtained was that of augelite, $Al_2PO_4(OH)_3$.

Chemical analyses of corrosion product from several samples in
this test (Table II) indicated iron and nickel concentrations significantly
greater than would be expected from the corrosion of X8001 aluminum.
The dark grey color of the corrosion product and the high iron and nickel
concentrations suggest that test equipment corrosion product (crud) had
deposited on the outer surface of the samples.

Table II

ANALYSES OF ALUMINUM CORROSION PRODUCT

Sample	Exposure Time, days	Al, w/o	Fe, w/o	Ni, w/o
122	119	22.9	15.1	3.8
118	223	21.9	14.7	4.0
115	277	25.6	13.9	3.6

Stainless Steel

Static: Samples of 18-8 stainless steels were exposed for periods of up to 182 days in helium-saturated phosphoric acid solution at pH 3 5 and 315°C Weight changes were as shown in Table III Data for type 347 are plotted in Fig 7

Table III

WEIGHT LOSS OF STAINLESS STEEL SAMPLES EXPOSED TO
pH 3 5 H_3PO_4, 315°C, He SATURATED

| Sample	Total Weight Loss in mg/cm^2 at Indicated Exposures						
Days Exposure	14	24	55	94	186		
Type 347 Annealed							
1) as pickled	-0 10	0 14	0 76	1 08	1 25		
2) as pickled	-0 07	0 15	0 73	1 03	1 19		
3) wet ground	-0 07	0 13	0 80	1 11	1 36		
4) wet ground	-0 03	0 11	0 87	1 24	1 43		
Type 347 Sensitized							
5) as pickled	-0 03	0 13	0 95	1 21	1 50		
6) as pickled	-0 19	0 15	0 97	1 26	1 44		
7) wet ground	-0 09	0 12	0 75	1 13	1 37		
8) wet ground	-0 07	0 19	0 86	1 26	1 54		
Type 316 Annealed							
1) as pickled	-0 04	0 05	0 81	1 16	1 32		
2) as pickled	-0 04	0 09	0 88	1 27	1 63		
3) wet ground	-0 04	0 01	0 73	1 07	1 15		
4) wet ground	-0 03	0 02	0 57	0 92	1 13		
Type 316 Sensitized							
5) as pickled	-0 07	0 35	1 55	2 21	2 15		
6) as pickled	-0 11	0 58	0 89	-	-		
7) wet ground	-0 07	0 07	0 53	0 93	1 05		
8) wet ground	-0 12	0 03	0 70	1 02	1 20		
Type 304 Annealed							
1) as pickled	-0 07	0 10	0 78	1 21	1 20		
2) as pickled	-0 10	0 09	0 63	1 03	1 30		
3) wet ground	0.15	0 11	0 55	0 84	0 82		
4) wet ground	0 13	0 17	0 03	0 18	0 10		
Days Exposure	10	31	41	70	81	158	168
Type 304 Sensitized							
5)	0 11		0 77		1 09		1 02
6)		0 58		0 81		0 88	
7)	0 12		0 74		1 12		1 11
8)	0 25		0 74		1 06		1 07
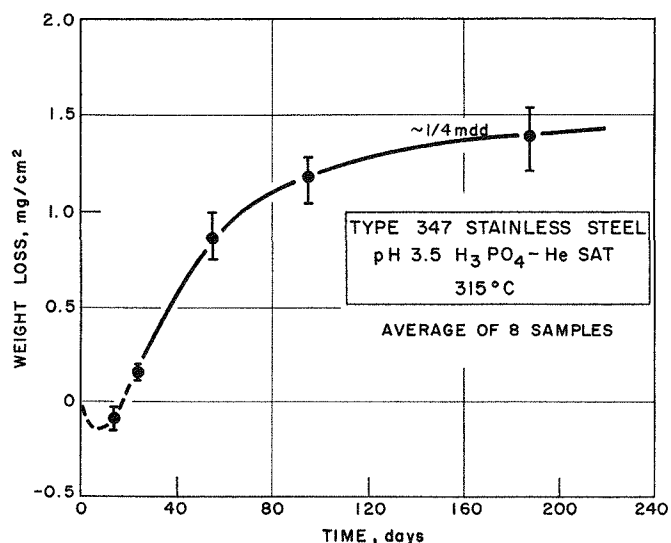
Fig. 7. Corrosion of Type 347 Stainless
Steel in Dilute Phosphoric Acid

The samples were covered with a dark thin film. There was some evidence of a small amount of loose crystalline deposit but no evidence of localized attack, such as pitting. The crystalline deposit was brushed off with Kleenex before weighings. The attack rate (Fig. 7) of $\frac{1}{4}$ mdd appears to be 10 to 100 times greater than for distilled water. The uncertainty is due to the lack of data for refreshed water at the same conditions of temperature and oxygen content. The phosphoric acid rate chosen represents a penetration rate of about 5×10^{-5} inch per year and cannot be considered alarming.

Post-corrosion metallographic examination revealed localized intergranular attack only on the sensitized type 316 samples (Fig. 8). The annealed type 316 specimens showed only a very slight tendency toward preferential grain boundary attack.

A similar test with fewer samples was performed at 225°C in helium saturated phosphoric acid. The results are shown in Table IV.

At about 40 days, samples had very light temper films ranging from almost metallic to light blue. At about 80 days, samples were covered with a thicker temper film, but one sample in the pH 3.5 acid had an area ($\sim$ 4 cm^2) of slightly darker and heavier film. No pitting was noted. Weight changes were of the same magnitude as those observed in distilled water.

26904   500X   26906   500X
        Annealed   Sensitized
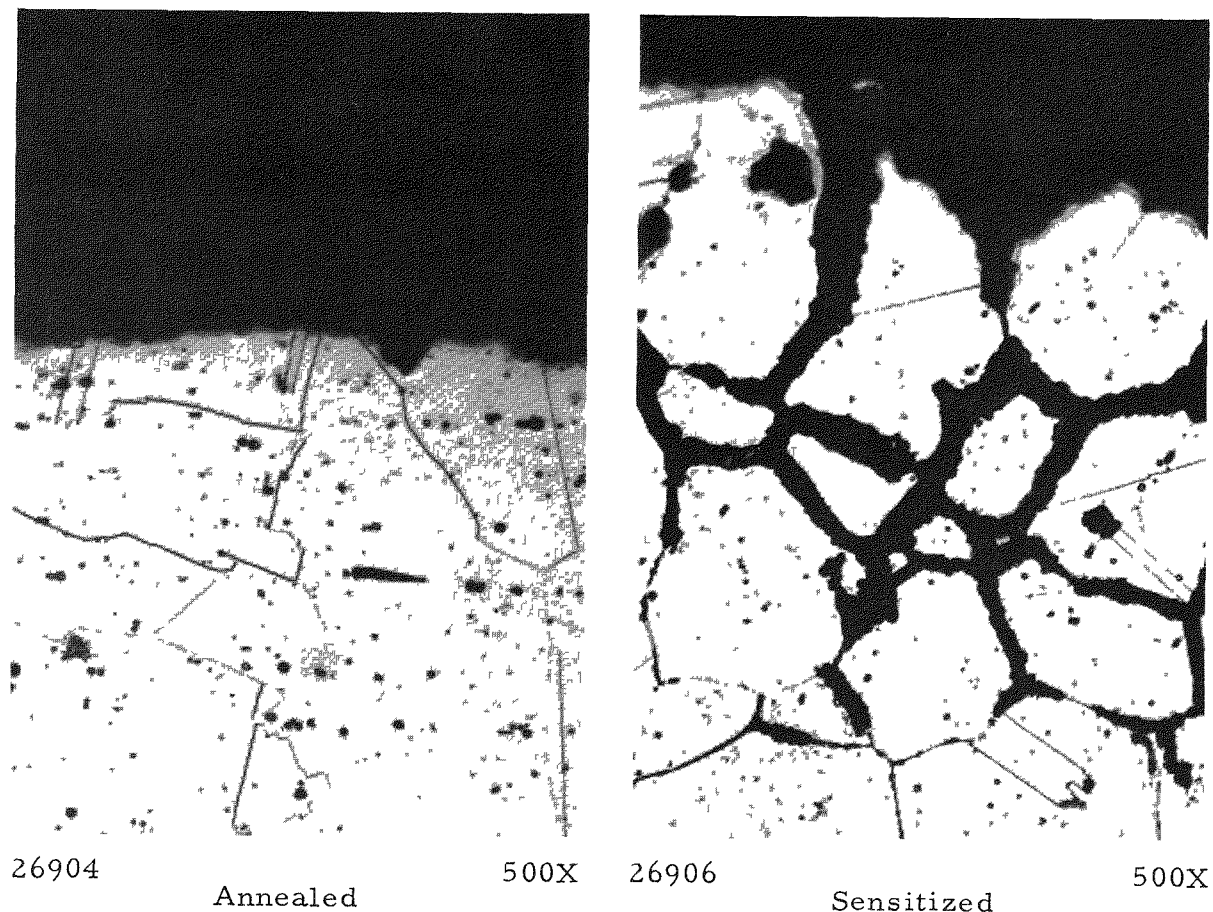
Fig. 8. Intergranular Attack of Sensitized Type 316 Stainless Steel
         Corroded in pH 3.5 Phosphoric Acid at 315°C for 186 Days

Table IV

CORROSION OF TYPE 347 STAINLESS STEEL SHEET
(AS RECEIVED) IN DILUTE PHOSPHORIC
ACID AT 225°C

Time, days	pH	Weight Loss, mg/cm^2
47	3.5	0.02
87	3.5	0.05
40	4.0	<0.01
80	4.0	<0.01

Dynamic Test: A dynamic test was performed on type 316 and 347
stainless steel sheet at 260°C in pH 3.5 H_3PO_4. No heat treatment was per-
formed; surfaces were wet ground (240 grit). Velocities were 2 and
22 ft/sec. The weight changes are presented in Table V.

Table V

WEIGHT LOSS OF STAINLESS STEEL; 260°C; pH 3.5 H_3PO_4*

Sample	Velocity, ft/sec	Total Weight Loss, in mg/cm², at Indicated Exposure Times, days				
		9.0	14.8	22.6	29.4	38.1
316-1	22	0.04	0.05	0.06	0.06	0.06
2	22	0.05	0.06	0.07	0.06	0.06
3	2	0.06	0.07	0.09	0.09	0.09
4	2	0.07	0.08	0.09	0.09	0.09
347-1	22	0.03	0.05	0.05	0.05	0.05
2	22	0.03	0.04	0.03	0.04	0.04
3	2	0.07	0.08	0.09	0.10	0.10
4	2	0.06	0.08	0.09	0.10	0.09

*Refreshing solution was saturated with hydrogen at 200 psi.

The samples exposed at 22 ft/sec had thin, multicolored films that persisted essentially unchanged throughout the test. The specimens in the slower stream changed from multicolored at nine days to a dull gold by the end of the test. The fact that the films are obviously thin, coupled with the low total weight loss, indicated a very low corrosion rate, of the same order as obtained in distilled water.

Obviously, the stainless steel dynamic loop used to contain the aluminum specimens for the 307-day test in pH 3.5 phosphoric acid at 315°C was also exposed to this environment. No weight change evaluation was made, but it is significant that no operating difficulty after the break-in run was attributable to the phosphoric acid. Trouble was experienced with the nickel bearing labyrinth during break-in. The nickel was so severely attacked that a replacement with a stainless steel labyrinth was necessary.

One section of the loop piping containing a welded type 304 orifice was removed and sectioned at the conclusion of the 307-day test. No intergranular attack was noted at any point. The appearance was comparable to that typically observed in pure water tests, indicating no abnormal corrosive attack occurred.

Aluminized Carbon Steel

Two completely clad (by spray aluminizing) specimens and sections of other coated specimens with one face of carbon steel exposed have been

The samples were covered with the usual smooth black film. Uncertainty in the amount of corrosion product retained during these tests makes it impossible to compare corrosion rates in phosphoric acid solution with those in water.

Thermal Stability of Phosphoric Acid Solution

A boiling experiment was performed to give preliminary information as to whether thermal decomposition or volatility would complicate the use of phosphoric acid solution in boiling reactors. An electrically heated stainless steel autoclave, of 6-in. ID and 18 in. tall, was half filled with solution and 2 kw of heat supplied. At temperature (252°C, 600 psia), thermal equilibrium was established by bleeding and condensing the steam at the rate at which it was produced. The condensed steam was tested for pH and resistivity. This condition of thermal equilibrium was maintained for about 30 minutes. At the end of this period the steam bleeding was stopped and the autoclave was maintained at 250°C for an additional 4 hours to see if thermal decomposition of the phosphoric acid produced any volatile components. The steam was again bled at the equilibrium rate to distill these components if present. Condensate measurements are presented in Table VII.

Table VII

CONDENSATE FROM pH 3.5 H_3PO_4 (250°C, 600 psia)

Test	Rate (lb/hr)	pH at 20°C	Specific Resistance, (ohm-cm at 20°C)
Initial Equilibrium	3.6	5.7	1,300,000
After $4\frac{1}{2}$ hours at 250°C	3.6	5.7	1,300,000

A previous 1-hour run with distilled water produced a gradual cleanup of the system, with a terminal value of 450,000 ohm-cm specific resistance and pH of 5.5. Measurements of the first distillate with the H_3PO_4 solution showed essentially these same values. Within 15 minutes the specific resistance had exceeded 1 megohm, indicating that the cleanup was completed. For the next 15 minutes the values shown in the table for initial equilibrium were obtained.

The data indicate that the relative volatility of H_3PO_4 was very low under these operating conditions and that thermal decomposition to volatile products did not occur in this length of time.

also shown intergranular attack according to the results of workers at Hanford. Our tests did not confirm this, either in a static system with sensitized samples or in a dynamic system with a welded specimen. Until the factors involved are better understood, the use of type 347 would seem prudent as it has a good corrosion record both here and at Hanford in dilute phosphoric acid.

Aluminized Carbon Steel

The use of properly heat treated aluminized carbon steel appears to combine the advantages of the low corrosion rate of aluminum with the low cost of carbon steel. Both crud formation and penetration rate would be higher in the case of a pinhole through the aluminum, but our preliminary tests did not indicate that they would be dangerously high.

Zirconium

Zirconium alloys were not attacked in any unusual fashion in this environment, suffering weight changes of the same order of magnitude as in distilled water.

Thermal Stability

At 252°C, 600 psi, there was no tendency for the dilute phosphoric acid to produce volatile components or to carry over into steam condensate. Unfortunately, the autoclave available did not adequately represent a scaledown of an operating boiling water reactor, such as the EBWR. For example, at 60,000 lb/hr, the EBWR has a rate of liberation of steam in the vessel of 50 lb per minute per square foot of water-steam interface. The autoclave provided a rate of only 0.3 in the same units. Due caution should therefore be exercised in extrapolating the boiling autoclave data to an operating boiling reactor.

CONCLUSION

Most of the common reactor metals investigated corroded at acceptably low rates in dilute phosphoric acid (pH 3.5). It would obviously be unsafe to generalize this statement to include other untested components.

Nickel and sensitized type 316 stainless steel were severely attacked by this solution at 315°C.

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