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UNIFORM AQUEOUS CORROSION OF ALUMINUM -
EFFECTS OF VARIOUS IONS

By

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UNIFORM AQUEOUS CORROSION OF ALUMINUM -
EFFECTS OF VARIOUS IONS

INTRODUCTION

Aluminum alloys have a high degree of corrosion resistance in water over a wide range of temperatures. For this reason, they have received widespread application in heat exchangers where the heat transfer medium is water. Nuclear reactors using water as a coolant are prominent examples. For this application, aluminum alloys must be able to withstand the corrosive effects of water at elevated temperatures for long periods of time.

There are three distinctly different types of aluminum corrosion. Uniform or general corrosion is the most destructive form at temperatures ranging from about 50° C to 250° C. This form of corrosion is characterized by an evenly distributed attack over the aluminum surface. At lower temperatures, pitting is the most destructive form of corrosion. It is characterized by areas of localized attack which result in pits or craters in the aluminum surface. At higher temperatures, intergranular penetration is the most destructive form of corrosion. Highly localized attack at the grain boundaries of the aluminum causes deep local penetration and rapid destruction of the physical properties of the metal. The uniform corrosion which occurs in conjunction with pitting attack and intergranular penetration is of minor importance in comparison to the localized corrosion.

Until recently, little work has been done on uniform aluminum corrosion. There has been a good deal of work done on pitting corrosion and intergranular corrosion as well as some work on the uniform corrosion in concentrated solutions of various acids and salts. There has been almost no work done, however, on the uniform corrosion of aluminum in dilute aqueous solutions because it was of minor importance compared to the other types. But because of the increased significance of uniform aluminum corrosion, particularly in high temperature nuclear reactors, increasing interest has been shown.

This report is limited to a study of the uniform corrosion process which occurs in the absence of localized attack. The objectives of the study are: (1) to provide a comprehensive synthetic survey of the effects of various ions and combinations of ions upon the uniform aqueous corrosion of aluminum, (2) to distinguish between ion effects and pH effects, and (3) to determine the suitability of short term corrosion tests at atmospheric pressure for investigating aqueous corrosive media.

SUMMARY

The most important variable in water quality on the uniform corrosion of aluminum was the pH. Solutions of distilled water containing phosphate ions and citrate ions were the only media which showed a definite specific ion effect. Phosphate inhibited the corrosion and citrate increased it. Oxalate ions appeared to increase corrosion, but the effect is not definitely demonstrated by the data. Corrosion was dependent only on pH in tap water, reactor process water, distilled water, and distilled water containing up to 100 ppm of chloride, nitrate, sulfate, bicarbonate, hydrogen peroxide, acetate, arsenate, silicate, dichromate, molybdate, and mixtures of these ions. Solutions of up to 10,000 ppm chloride in distilled water showed no specific ion effect upon uniform aluminum corrosion.

The effects of 0-10 ppm of dichromate and phosphate ions were investigated over the range pH 4 to pH 7. Phosphate at 10 ppm inhibited corrosion in solutions containing up to 2 ppm of dichromate, but at 10 ppm dichromate the phosphate does not appear to inhibit corrosion. Also at 10 ppm dichromate, the effect of pH is diminished over the range pH 4 to pH 7.

Corrosion rates varied with the flow rates of the test solutions at low flow rates, and were lowest at the lowest flow rates. This effect was attributed to the buildup of aluminate ion concentration in the lower flow systems.

Short term corrosion tests at 92°C revealed major specific ion effects. Minor effects were lost in experimental uncertainties. The inhibiting effect of phosphate under these conditions has been shown to exist over longer exposures at higher temperatures.

DISCUSSION

Literature Survey

Considerable investigation has been conducted to ascertain and evaluate the parameters of aqueous aluminum corrosion.^(1, 2) Parameters of importance in one form of corrosion are not necessarily of importance in the other forms of corrosion. The concentrations of chloride and bicarbonate ions have been shown to be important parameters in pitting corrosion,^(3, 4) but these are less important in uniform corrosion. The composition of the aluminum alloy, which is not an important parameter in uniform corrosion,⁽⁵⁾ is important in pitting and intergranular penetration corrosion.⁽⁶⁾

The most important parameters of uniform aluminum corrosion are temperature, time, water composition, and flow rate. The corrosion rate is highly dependent upon the temperature and increases rapidly with increasing temperature. Under static or low flow conditions, the rate of uniform corrosion decreases parabolically with time because of the accumulation of a protective film of corrosion product. In some cases, where the corrosion product film is removed or changed by the corrosive environment, a constant equilibrium corrosion rate is established after the initial exposure period. The composition of the water in which aluminum is corroded has a marked effect upon the corrosion rate.

Water composition is generally the most difficult parameter to control,^(5, 7) and variations in water composition are the source of much of the non-reproducibility of results obtained in corrosion studies. A good deal of work has been done to determine the important factors in water composition. Much of this work has been analytical; that is, a correlation attempted

between variations in corrosion rates and variations in the chemical analysis of the water in which the aluminum corroded. The greatest difficulty with the analytical approach to this problem is that the effects of so many variables are combined and confounded that it is extremely difficult to ascertain the important ones.

Another serious difficulty arises from the absence of systematic experimental planning. That is, the corrosion experiments are conducted in water of uncontrolled composition resulting usually in an inadequate sampling from the population of all possible waters. These unsystematic measurements do not yield to efficient methods of data analysis such as cross-plotting or analysis of variance.

The alternative approach, used in this study, is a synthetic method in which solutions of various ions and combinations of ions in high purity water are used as corrosive media. The water composition can be controlled and the experimental observations made in a systematic fashion which will yield to efficient methods of data analysis.

It is difficult to resolve and correlate much of the pertinent information because of the wide variation in corrosion testing procedures and conditions and because of the existence of uncontrolled or undefined variables. For instance, it appears that some effects attributed to specific ions were probably caused by differences in pH or type of corrosion. There is some disagreement as to whether the velocity at which the solution flows past the aluminum has an effect. These discrepancies might be caused by differences in the design of the testing facility or failure to recognize some uncontrolled variable such as pH or the concentration of dissolved aluminum. The information in the literature is best considered by organizing it with regard to the important factors in uniform aluminum corrosion.

a. Time

Because the corrosion rate of aluminum is controlled in some manner by the buildup of a corrosion product film on the surface, it was expected that the corrosion rate would decrease with time. Indeed, it has been shown

by Dillon⁽⁸⁾ that under conditions of low flow and high temperature in high purity water the corrosion rate decreases parabolically with time. Under many conditions, however, the corrosion does not proceed in this ideal parabolic manner. At lower temperatures, about 150°C or less, the corrosion frequently proceeds very rapidly at first and then continues at a very low and often immeasurable rate. This has been observed in tap water at 90°C⁽⁷⁾ and in nearly neutral high purity water up to 150°C^(9, 10).

If the corrosion occurs under conditions of high flow or in solutions which are detrimental to the corrosion product film, a steady state can be reached where the protective corrosion product is formed and destroyed at the same rate, giving rise to a constant linear rate of corrosion. Linear corrosion rates have been observed by Groot and Peekema⁽⁵⁾ in reactor process water up to 120°C and by Lobsinger and Atwood⁽¹¹⁾ in high purity water at flow velocities of 10 to 20 feet per second and temperatures up to 250°C.

Several investigators^(12, 13, 14) have attempted to fit an empirical equation to the in-reactor corrosion data at Hanford. Although they recognized the existence of a rapid initial corrosion, the exposure times were sufficiently long that the initial corrosion was only a small portion of the total corrosion and a linear corrosion rate could be assumed. It has also been observed recently⁽¹⁵⁾ that in some instances the corrosion follows an inverse logarithmic law, where the initial corrosion rate is very high and rapidly falls off to nearly zero.

b. Temperature

In his summation of much of the early aluminum corrosion work at Hanford, Kidder⁽¹⁶⁾ stated that the logarithm of the corrosion rate is proportional to the reciprocal of the absolute temperature. This is what would be predicted from the Arrhenius equation.⁽¹⁷⁾ Dillon⁽⁸⁾ and Draley⁽⁹⁾ have supported this conclusion. It was shown by Groot^(4, 5) and Draley⁽⁹⁾ that this relationship does not hold strictly at temperatures less than 150°C although their results do not agree with regard to the direction of deviation.

Some low temperature corrosion data^(5, 10) have failed to show any temperature dependence probably because of experimental limitations. In summarizing in-reactor corrosion data, Woods⁽¹²⁾ reported that the logarithm of the corrosion rate was proportional to the temperature. deHalas⁽¹³⁾ and Groot⁽¹⁴⁾ showed that the logarithm of the corrosion rate was proportional to the reciprocal of the absolute temperature, although Groot found that the constant of proportionality differed for different temperature ranges.

c. Alloy

Although there are considerable differences between aluminum alloys with regard to localized corrosion,⁽⁶⁾ there is little difference with regard to uniform corrosion. Kidder⁽¹⁶⁾ reported that 2S and 72S corroded at the same rate, but an alloy containing 13 per cent silicon corroded 2 to 3 times faster. Lobsinger and Atwood⁽¹¹⁾ found no difference in corrosion rate between alloys M388, M400, X2219, and 1100. Groot and Peekema⁽⁵⁾ found no significant difference between a wide variety of alloys with the possible exception of 24S, which contains 4.5 per cent copper.

d. Surface Preparation

Kidder⁽¹⁶⁾ reported that neither the rate nor the type of corrosion was dependent upon the surface preparation of aluminum corrosion samples. There was no detectable difference in corrosion between new surfaces and scratched, etched, or abraded surfaces. This would probably not be the case when very small amounts of corrosion were to be measured since abrasion would increase the sample surface area to an unknown and variable extent.

e. Flow Velocity and Surface to Volume Ratio

Dillon⁽⁸⁾ has found that corrosion which occurs in static systems is only half that which occurs in low velocity flowing systems. Miller and Lobsinger⁽¹⁸⁾ also have shown an increased corrosion rate with increased velocity. Kidder⁽¹⁶⁾ states that there is no observable difference between flow velocities of 5 to 20 feet per second. Dillon⁽⁸⁾ and Miller⁽¹⁸⁾ have suggested that the difference between static and low flow testing conditions

may be attributable to a difference in the buildup of dissolved aluminum concentration or a common ion type of effect. If the common ion effect does exist, then increasing the aluminum concentration would decrease the corrosion of aluminum. Dillon and Lobsinger⁽¹⁹⁾ have reported a decrease in corrosion by a factor of three as a result of increasing the exposed aluminum surface area in a dynamic test facility.

Since the surface area of aluminum to solution volume ratio does affect the corrosion rate, it is clear that there is an interaction between the effects of flow velocity and the physical dimensions and design of the corrosive environment upon the corrosion of aluminum. Draley⁽²⁰⁾ has shown an interaction between the effects of solution pH and flow velocity. Because of these interactions, it is difficult to correlate the corrosion data obtained from different sources and test facilities.

f. pH and pOH

There is general agreement on the effect of pH on the corrosion of aluminum^(9, 11, 16, 18, 19, 20, 22, 23, 24, 25). At a given temperature and under a given set of environmental conditions, there is a pH of minimum corrosion. At higher or lower values of pH, the corrosion is increased markedly. Quantitative assessment of the effect of pH is difficult because of the environmental interactions mentioned in the previous section and the experimental difficulties encountered in measuring the pH. It is a simple matter to make up a solution and adjust it to a desired pH at ambient conditions. It is very difficult, however, to adjust the ambient pH in a manner which will result in a desired pH when the solution is heated. Indeed, if the solution is heated to a temperature above 100° C, it is almost impossible to measure the pH of the hot solution. Also, it is very difficult even to predict the pH of the hot solution from its ambient pH since the pH of the hot solution is dependent upon the composition of the ambient solution and the conditions under which it is heated. For instance, Houck⁽²¹⁾ reported that the pH of alum treated

reactor process water decreased from pH 7.7 to pH 6.7 upon increasing the temperature from 8° C to 80° C.

Most investigators measure the ambient pH of their test solutions, but many fail to specify the manner or temperature of the pH measurement. The aluminum corrosion process is dependent upon the conditions existing in the hot solution in which the aluminum is corroded. Consequently, the pH of the hot solution is undoubtedly more significant than the ambient pH of the solution. Since the pH of the hot solution is dependent on the composition of the solution as well as the conditions and duration of heating, there must be a complex interaction between the ambient pH of a solution, the solution composition, flow rate, and environment design.

Draley and Ruther⁽⁶⁾ have shown that the pH of minimum corrosion decreases with increasing temperature. Carlsen⁽²³⁾ has pointed out that solutions of a highly dissociated acid maintain an essentially constant pH with increasing temperature while the pOH decreases. He concluded that the hydroxyl ion concentration was more significant than the hydrogen ion concentration, and that it is therefore necessary to decrease the ambient pH of a solution in order to maintain the proper pOH at elevated temperatures.

Another problem which arises in evaluating the effect of pH on aluminum corrosion is the difficulty in distinguishing between a pH effect and the effect of some other ion present. For example, Miller and Lobsinger⁽¹⁸⁾ have shown a decrease in corrosion in going from high purity water at pH 5.9 to high purity water with sufficient nitric acid to give pH 5.3, to high purity water with sufficient phosphoric acid to give pH 4.5. Without additional tests it is difficult to say whether the reduction in corrosion is a result of reduced pH, or an effect of phosphate or nitrate ions, or a combined effect of pH and phosphate or nitrate ions.

In their treatments of the reactor corrosion data, Woods⁽¹²⁾ and deHalas⁽¹³⁾ did not include the parameter of pH since it sufficed to consider corrosion data at a single value of pH. Groot and Wilson⁽¹⁴⁾ had sufficient data to include the pH parameter, and they concluded that the logarithm of the corrosion rate was proportional to the pH.

g. Water Composition

There are many scattered references to the effect of various dilute aqueous solutions on the corrosion of aluminum. In some cases, disagreement between investigators is probably a result of uncertainties in pH measurement and test conditions. Kidder⁽¹⁶⁾ reported no effect caused by sodium silicate over the range of 0 to 70 parts per million (as SiO_2), no effect of chloride at less than 4 ppm (although he states that chlorides are very corrosive to aluminum), and no effect of hydrogen peroxide over the range of 0 to 500 ppm. He also found no difference between demineralized water and reactor process water. He reported that 53 ppm of oxalic acid at pH 3.5 and 95° C was very corrosive, and that sodium dichromate over the range of 1 to 20 ppm inhibited corrosion, although no correlation could be found between the amount added and the degree of inhibition.

Miller and Lobsinger⁽¹⁸⁾ have found that nitric acid and phosphoric acid additions to high purity water inhibit aluminum corrosion. They attribute the inhibition in the first case to a lowering of the pH rather than the presence of nitrate ions. In the second case, the inhibition is attributed to the presence of phosphate ions.

Draley et al⁽²⁵⁾ reported the following: (1) chloride ion above 2 ppm increased the corrosion at 70° C and 95° C, (2) hydrogen peroxide had no significant effect up to 35 ppm, (3) calgon (sodium polyphosphate) at 3 to 11 ppm increased corrosion, (4) Kimerly-Clark waste sulfite liquor at 5 ppm caused a considerable increase in corrosion, (5) Texas soluble oil C had no effect up to 7 per cent, (6) sodium nitrate and sodium nitrite up to 14 ppm had no effect, (7) calcium and magnesium sulfates (20 ppm Ca^{++} , 6 ppm Mg^{++}) showed no consistent effect, and (8) dissolved oxygen had no effect.⁽²⁷⁾ It is quite possible that in some of the cases of increased corrosion the effect actually being observed was due to pH changes. Draley and Ruther⁽⁹⁾ found the addition of oxygen (saturated) and hydrogen peroxide (35 ppm) inhibited corrosion at 70° C, while 100 ppm of sulfate increased the corrosion rate by a factor of five at pH 7 and 50° C.

Mears⁽²⁸⁾ observed that heavy metal salts greatly increase the rate of aluminum corrosion in acid solutions but not in alkaline solutions. Carlsen⁽²⁹⁾ reported that 0.5 per cent potassium dichromate plus 0.5 per cent sodium silicate is a good inhibitor. He also stated⁽²³⁾ that one per cent potassium dichromate inhibits corrosion of aluminum.

Planning

The major problem which is immediately apparent when considering a project in which a large number of variables and combinations of variables are to be evaluated, is the very large number of experiments which must be performed. For example, if the effect upon the corrosion of aluminum were to be determined for solutions of 10 different ions and all their combinations at two levels of concentration, (for example, 0 and 100 ppm) the total number of tests required would be 1024. If these solutions were to be studied at 5 different levels of pH, then the number of experiments is 5,120. Again, if two different alloys of aluminum are to be included in the survey, then 10,240 experiments would be required. If it requires a month per test to determine corrosion rates and if 50 tests can be performed at the same time (conditions which are very optimistic for most corrosion studies), then the total time required to complete such a program would be 17 years. The survey program undertaken here was reduced to a more reasonable length of time by running as many simultaneous experiments as possible, by reducing the duration of each test as much as possible, and by making several assumptions based on previous aluminum corrosion experiences.

It was first necessary to decide on how many experiments could be performed at the same time and for how long and at what temperature. The maximum temperature which can be conveniently maintained in aqueous systems at atmospheric pressure, without seriously high evaporation rates, is about 90° C. It has been observed that at temperatures of about 90° C most of the corrosion occurs during the first two weeks of exposure^(7, 10) and, consequently, more information can be gained from many short term

tests than from fewer tests of longer duration. The cells in which the aluminum samples were corroded were made as small as possible to allow frequent changes of solution without requiring a very large feed water supply. Frequent changes of solution were desired in order to maintain a constant composition of the solution about the corrosion samples. Available space, personnel, and equipment limited to fourteen the number of experiments that could be performed simultaneously.

Because of the limitations on temperature and duration of each test, it was realized that only gross effects would be significant. That is, only the ions or combinations of ions which have a great effect upon aluminum corrosion could be demonstrated to have an effect. Also, it was realized that only the direction and not the magnitude of gross effects would be significant. It was also felt that the effects observed during the two weeks of exposure are representative of the effects which would be observed over a longer duration of exposure. In other words, only the ions which demonstrate a prominent corrosion inhibiting or enhancing effect are considered to have a specific ion effect, and it is believed that any such inhibiting or enhancing effect occurs over long duration exposures and probably at other temperatures provided that the corrosion is of the uniform type. For example, the corrosion inhibiting effect of phosphate ion has been demonstrated by Lobsinger and Atwood⁽¹¹⁾ over 1700 hours at 150° C and 250° C in a dynamic test facility at flow rates up to 20 fps. Their results are presented in Figures 1 and 2.

Figures 1 and 2 also show that there is very little difference, if any, between alloys of very different composition. This is in agreement with the work of Groot and Peekema⁽⁵⁾ which has shown that there is essentially no difference in the uniform corrosion characteristics of a large number of commercial aluminum alloys. Consequently, it was decided to use only one alloy throughout this testing program.

FIGURE 1
CORROSION OF ALUMINUM ALLOYS AT 150 C

FIGURE 2
CORROSION OF ALUMINUM ALLOYS AT 250 C

As the study progressed, the pH of the solution was found to be the most significant variable. Concentration was important only for the ions which enhanced or inhibited corrosion. It also appeared that simple combinations of ions had not produced any effects different from the effects of the ions alone. Indeed, the results given in Table V show essentially no difference between tap water, reactor process water, and distilled water from the standpoint of uniform corrosion at a given pH. For these reasons, as the work progressed, the number of different concentrations was limited and most of the simple combinations of ions were eliminated. In the cases where there appeared to be an inhibiting or enhancing ion effect, the effect was determined at a variety of concentrations and pH values. For example, phosphate demonstrated an inhibiting effect on uniform aluminum corrosion and tests were conducted at several pH values and phosphate concentrations. Also, since sodium dichromate is of such importance as a pitting corrosion inhibitor in reactors, ^(30, 31, 32) a 64 experiment test was performed involving 4 values of phosphate concentration (0, 0.5, 2, and 10 ppm), 4 values of dichromate concentration (0, 0.5, 2, and 10 ppm), and 4 values of pH (4, 5, 6, and 7).

Tests were run to show the effect of reducing the solution flow rate from low flow to nearly zero. Extended exposure tests were run to demonstrate the continuity of effect with solutions showing a specific ion effect.

When it became apparent from the data obtained that there is a pH of minimum corrosion at 92° C, tests were made to determine the effect of temperature on the pH of minimum corrosion. Aluminum coupons were exposed to buffer solutions of pH 3 to 8 at temperatures up to 305° C in a high temperature, high pressure autoclave.

Procedure

The apparatus used for this survey is shown in Figures 3, 4, 5, and 6. The samples used were 1/2 inch by 2 inch coupons of 245 aluminum cut from 1/16 inch sheet taken from the same lot of stock. Each sample had

FIGURE 3

CORROSION TESTING APPARATUS

Assembled

Disassembled

FIGURE 4

CORROSION CELL

FIGURE 5

CORROSION TEST FACILITY

FIGURE 6

CORROSION TEST FACILITY

an area of 14.3 square centimeters. Alloy 1245 is Hanford can stock with a nominal composition of 99.45 per cent aluminum with the iron and silicon content controlled. All the coupons were degreased in acetone and annealed at 600° C for 10 minutes. No other sample preparation, such as abrading, was used since degreasing and annealing more closely duplicated reactor service conditions.

Four coupons were weighed and suspended within each of the corrosion cells. The cells were then immersed in a constant temperature water bath at 92° C. A temperature recorder on the bath indicated no significant variations in bath temperature. A partial cover and a layer of light oil on the surface of the bath minimized evaporation losses from the bath.

The various corrosive media to be studied were made up in 5-gallon bottles. The pH was measured with a Beckman Model H-2 glass electrode pH meter at room temperature (about 22° C) and is hereinafter referred to as the "cold pH" or "initial pH". The solutions were siphoned through the corrosion cells at a rate of about 50 ml per hour. The corrosion cells contained about 25 ml of solution about the samples. Thus, the feed water supplies lasted the required two weeks without refilling and the solution surrounding the corrosion samples was changed every half hour.

The flow rate was maintained by means of the flowrator and micro-flow regulator. The microflow regulator consisted of a piece of 0.016 inch diameter stainless steel wire inserted into a length of capillary tubing. The flow rate was adjusted by moving the wire into or out of the capillary. The capillary was carefully selected to give the desired range of flow rates. A glass wool filter in the delivery line excluded small particles of foreign matter from the flowrator, regulator, and corrosion cell. A thermometer inserted in the center tube of the corrosion cells indicated that the temperature of the cell contents was the same as the bath temperature. Several preliminary cell designs were discarded because of a large temperature difference between the cell contents and the bath.

After an exposure period of 308 hours (a period of a little less than two weeks), the corrosion cells were removed from the bath and the pH values of the hot solutions were measured. This pH, measured at about 80° C, is hereinafter referred to as "hot pH". The cells were then degreased in a trichloro ethylene vapor degreaser to remove the oil picked up from the bath. The sample coupons were dried in air and weighed. They were then stripped of their corrosion product film by heating in 2 per cent chromic - 5 per cent phosphoric acid in a pressure cooker at 15 pounds pressure for one hour, and weighed again. Within the experimental error of weighing, ± 0.1 mg, there is no measurable loss in weight because of stripping or because of oxide present initially on the samples. This was shown in an experiment in which ten aluminum coupons were annealed and stripped by the same procedure as used for the sample coupons. The results of this test are shown in Table I.

TABLE I
WEIGHT LOSS BECAUSE OF STRIPPING AND INITIAL OXIDE FILM

<u>Sample</u>	<u>Weight Loss During Stripping</u>
1	0.1 mg
2	0.1
3	0.0
4	0.2
5	0.0
6	0.1
7	0.1
8	0.1
9	0.1
10	0.2

The extent of corrosion was measured by the difference between the initial sample weight and the weight after stripping. The weight losses were averaged for the four samples in each corrosion cell. Because the

weight was uniformly lost from the samples, the weight loss data was converted to units of penetration by the following calculations:

$$\frac{(\text{Average Weight Loss}) (.394)}{(\text{Sample Area}) (\text{Density of Sample})} = \text{Average milli-inches penetration}$$

Since for all the samples the area was 14.3 cm^2 and the density was 2.7 gm per cm^3 , the calculation became

$$(\text{Average Weight Loss}) (0.0102) = \text{Average milli-inches penetration}$$

In the extended exposure experiments, one of the four aluminum coupons in each cell was removed for weighing and stripping after 163, 308 and 716 hours exposure. A fresh aluminum coupon was replaced in the cells at these times. The three replacement coupons and the fourth original coupon were removed after the original coupon had been exposed for 1025 hours.

The apparatus used for the determination of the effect of temperature on the pH of minimum corrosion is shown in Figures 7 and 8. Two aluminum coupons were placed on a stainless steel wire support in each of six small stainless steel capsules. The capsules were $2/3$ filled with the desired buffer solutions and sealed with a stainless steel cap and an annealed aluminum gasket. The six capsules were then placed in a rack within the larger autoclave which was half filled with water. The autoclave was maintained at the desired temperature by automatic controls. Because the pressure built up within the autoclave was about the same as that in the capsules, there was no danger of the solutions leaking out of the capsules. After the desired exposure period the samples were removed from the autoclave and weighed.

Because the corrosion product formed above 100°C does not yield readily to chromic-phosphoric acid stripping, it was necessary to dissolve the aluminum metal and weigh the remaining corrosion product to obtain the weight loss data. The method was described by Pryor and Keir⁽³³⁾ and involved refluxing the corrosion samples in a solution of iodine in methanol

FIGURE 7

HIGH TEMPERATURE APPARATUS

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FIGURE 8

HIGH TEMPERATURE AUTOCLAVE FACILITIES

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until the metal is completely dissolved. The difference between the weight of the corroded sample and the weight of the corrosion product gives the weight of the aluminum metal after exposure. The alloy initially used was 1245, but because of the occurrence of intergranular penetration corrosion at elevated temperatures, the alloy M388, which contains one per cent nickel and is highly resistant to this type of corrosion, was used for later experiments.

Results

a. Effects of pH

The aluminum coupons were exposed to tap water, reactor process water, and distilled water solutions of various ions and combinations of ions. The solutions ranged from pH 2 to pH 10. The experimental data are given in Table V. Unless otherwise indicated, the solutions were prepared from the sodium salts of the anions in distilled water. Sodium hydroxide or sulfuric acid was added in the cases where the pH of the solutions was adjusted to a desired initial value.

The pH of the solution was the most important parameter in the uniform aqueous corrosion of aluminum, and all weight losses were correlated with pH. The best correlation was obtained by using the pH values of the hot solutions. This is reasonable since the hot pH most closely indicates the pH at which the sample corroded. This correlation is shown by curve A of Figure 9. The regression lines drawn through the data plotted in Figure 9 were obtained by using the method of least squares after making the observation that the data could be conveniently divided into two groups at pH 5.8. The relationship is probably more truly represented by the dashed line in Figure 9.

The effect of pH on the corrosion of aluminum is a result of the effect of pH on the solubility of the corrosion product film. This effect is shown in Figure 10 in which the logarithm of the ratio of the corrosion product film weight over the weight loss of the sample is plotted against the hot pH. The regression lines through the plotted points were calculated by the method of

FIGURE 9

CORROSION AS A FUNCTION OF pH

FIGURE 10

FILM WEIGHT/WEIGHT LOSS RATIO AS A FUNCTION OF pH

least squares. Here again, the relationship is probably more truly represented by the dashed line, which indicates not only a more gradual change from acid to basic dissolution of the corrosion product, but also a maximum ratio between the weight of the corrosion product and the weight of the corroded aluminum at the pH of minimum solubility. If the corrosion product was the monohydrated alumina, which contains 45 per cent aluminum, then the maximum ratio of film weight to weight loss would be 2.22, assuming no solubility of the corrosion product. For the trihydrated alumina, which contains 34.5 per cent aluminum, the maximum ratio would be 2.90. Even if the corrosion product films contained adsorbed water, which could increase the ratio, it is very doubtful that the ratio could truly be as high as that shown by the intersection of the two regression lines.

Comparison of Figures 9 and 10 shows the two curves to be almost identical. This would be expected if the effect of pH on the uniform corrosion is related to the effect of pH on the solubility of the corrosion product film. For example, at pH 9 the corrosion is high and the film weight to weight loss ratio is low, indicating that only a small fraction of the corroded aluminum remained on the samples as corrosion product. Minimum corrosion was observed at pH 5.6 and the film weight to weight loss ratio was about maximum, indicating that most of the corroded aluminum remained on the samples as corrosion product film.

The effect of pH on uniform aluminum corrosion may be considered in terms of the concept of protective film forming efficiency. The efficiency is a measure of the amount of protective corrosion product film formed by the corrosion of a given amount of aluminum. This efficiency is actually what is measured by the film weight over weight loss ratio. At high or low pH, the efficiency is low since a large amount of corrosion must occur to form a small amount of protective film. At the pH of minimum corrosion, the efficiency is high and a minimum amount of corrosion is required to form a protective film.

The reason for the difference between the initial pH and the hot pH is not clearly understood. There are several theories which can qualitatively explain most of the observations. As pointed out by Bryan,⁽²⁴⁾ aluminum corrosion in acid solutions produces an increase in pH and in basic solutions produces a decrease in pH. This can be explained by assuming the ionization of aluminum hydroxide in acid solutions to be

and in basic solution

If the corrosion process, or rather the dissolution of the corrosion product, was responsible for the difference in pH, then it would be expected that solutions initially at less than pH 5.8 would increase in pH and solutions initially above pH 5.8 would decrease in pH. In the instances where the solutions were reactor process water, tap water, or other solutions containing bicarbonate, the evolution of carbon dioxide upon heating would cause an increase in pH. In the data of Table V there are 82 tests given for which the initial and hot pH were recorded. Of these, 37 were initially below pH 5.8 and increased in pH, or were above pH 5.8 and decreased in pH. Of the 45 exceptions, 28 (marked**) were solutions containing bicarbonate above pH 5.8 that increased in pH upon heating. The 17 other exceptions (marked*) are unexplained. Data are given in Table VI for 64 tests involving solutions of phosphate and dichromate ions in distilled water. Of these 64 tests, 56 were initially below pH 5.8 and increased in pH or were above pH 5.8 and decreased in pH upon heating. The 8 exceptions (marked*) are unexplained.

b. Ion Effects

The only ions which demonstrated specific ion effects were citrate and phosphate. Citrate at 100 ppm enhanced the corrosion as indicated in Figure 9, and phosphate at 0.5 to 100 ppm inhibited the corrosion as shown by Curve B of Figure 9 and by the curve of Figure 11. Oxalate, which is

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FIGURE 11

PHOSPHORIC ACID INHIBITION IN REACTOR PROCESS WATER

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usually considered harmful to aluminum, did not show a definite ion effect. The corrosion enhancing effect of citrate is caused by the increased solubility of the corrosion product which is undoubtedly the result of the formation of an aluminum citrate complex.⁽³⁴⁾ The corrosion inhibiting effect of phosphate is believed to be caused by the formation of a basic aluminum phosphate corrosion product film rather than the usual hydrated alumina film. An attempt was made to identify by X-ray diffraction the film formed in phosphate solutions in this series of tests but this could not be accomplished because there was so little film formed under the conditions of these tests. However, a sample of the film formed in 5 ppm phosphoric acid at 195° C after an exposure of 24 days in a high flow rate test facility was analyzed by X-ray diffraction and was identified as augelite,⁽³⁵⁾

When this survey was first started, it was expected that the variations in the corrosiveness of process waters were due to variations in concentration of the anions commonly found. For this reason, the solutions studied contained anions in the range of concentration at which they occur in process waters. As the work progressed and many of the expected results failed to materialize, many of the experiments were repeated and tests involving additional concentrations and combinations were performed. For example, when a chloride ion effect was not found at 100 ppm, tests were run with concentrations up to 10,000 ppm. As more and more tests were run, it became apparent finally that the pH of the solution was the most significant variable. As a result, succeeding tests were run at fewer levels of concentration, and many of the possible combinations were replaced by a few tests involving the combinations of many ions.

None of the solutions listed in Table II showed a specific ion effect in these experiments. When considered at the same hot pH, there was no difference shown between distilled water and tap water (Table III) or reactor process water (Table IV).

TABLE II
TEST SOLUTIONS NOT SHOWING A SPECIFIC ION EFFECT

<u>Constituent</u>	<u>Maximum Concentration</u>
Distilled Water	
Chloride	10,000 ppm
Bicarbonate	100
Hydrogen Peroxide	100
Nitrate	100
Sulfate	100
Silicate	100
Dichromate	2
Acetate	100
Arsenate	100
Molybdate	100
Phosphate	0.1
Bicarbonate-Chloride	100 - 5
Hydrogen Peroxide-Chloride	100 - 100
Hydrogen Peroxide-Bicarbonate	100 - 100
Hydrogen Peroxide-Bicarbonate-Chloride	10 - 100 - 5
Nitrate-Bicarbonate	100 - 100
Nitrate-Chloride	100 - 5
Sulfate-Bicarbonate	100 - 100
Sulfate-Chloride	100 - 5
Chloride-Bicarbonate-Hydrogen Peroxide	
Nitrate-Sulfate	100 each
Silicate-Chloride	100 - 500
300 Area Tap Water	266 ppm Total Solids See Table III for analysis
Reactor Process Water	89.6 ppm Total Solids See Table IV for analysis

TABLE IIITYPICAL ANALYSIS OF 300 AREA TAP WATER

pH		8.0
Turbidity		0.3 ppm
Methyl Orange		182
Hardness		162.5
Total Solids		266
SO_4^{-2}		26
Cl		8.2
SiO_2		34
Fe		0.034
Cr^{+3}	Less than	0.002
Cu		0.010
Al	Less than	0.05
Mg		7.2
Ca		31.1

TABLE IVTYPICAL ANALYSIS OF REACTOR PROCESS WATER

pH		6.9
Turbidity		0.36 ppm
Methyl Orange Alkalinity		39.0
Hardness		72.1
Total Solids		89.6
SO_4^{-2}		12.8
Cl^{-}		0.9
SiO_2		7.8
Fe		0.046
Cr^{+3}		0.115
Cu		0.004
Al	Less than	0.002
Mg		4.0
Ca		22.3
$\text{Cr}_2\text{O}_7^{-2}$		2.0

TABLE V
CORROSION DATA

<u>Solution (ppm)</u>	<u>Average Penetration (mils/308 hours)</u>	<u>Avg. Film Wt. Avg. Wt. Loss</u>	<u>Initial pH</u>	<u>Hot pH</u>
Distilled Water	0.017	1.99	7.9	
	0.018	2.16		7.5
	0.016	2.25		6.4
	0.016	2.38		7.1
	0.039	1.23		8.0
	0.018	2.27		7.5
	0.024	1.56		7.7
	0.029	1.23		4.1
	0.016	2.06		4.3
	0.017	2.22		6.5
	0.016	1.76		7.2
	0.014	2.11	7.5	7.2
	0.016	1.69	7.6	7.1
	0.013	2.60	7.0	7.0
	0.009	2.53	6.1	6.4*
	0.005	3.11	5.1	5.9
	0.002	6.75	4.0	4.8
	0.011	2.12	5.4	6.9
	0.009	2.00	5.4	5.0*
	0.012	2.52	5.4	7.1
	0.014	2.15	5.4	4.9*
1 - Cl ⁻	0.014	1.78	7.9	
1 - Cl ⁻	0.018	2.22		7.5
1 - Cl ⁻	0.020	2.40		6.6
5 - Cl ⁻	0.026	2.19	7.5	
5 - Cl ⁻	0.023	2.13		7.4
5 - Cl ⁻	0.022	2.25		6.8
10 - Cl ⁻	0.026	2.18	7.6	
10 - Cl ⁻	0.024	2.16		7.5
10 - Cl ⁻	0.021	2.35		6.8

* See page 27.

TABLE V (contd.)

Solution (ppm)	Average Penetration (mils/308 hours)	Avg. Film Wt. Avg. Wt. Loss	Initial pH	Hot pH
50 - Cl^-	0.024	2.13	7.5	
50 - Cl^-	0.020	2.13		7.1
50 - Cl^-	0.020	2.26		6.7
100 - Cl^-	0.018	2.34		6.7
1,000 - Cl^-	0.018	1.59	5.6	6.3
10,000 - Cl^-	0.015	3.35	6.0	6.4*
10 - HCO_3^-	0.014	2.20	6.8	7.7**
50 - HCO_3^-	0.048	1.38	7.0	8.2**
100 - HCO_3^-	0.066	1.20	7.5	8.3**
100 - HCO_3^-	0.059	1.26		8.7
100 - HCO_3^-	0.021	2.35		7.2
100 - HCO_3^-	0.102	1.07		9.2
100 - HCO_3^-	0.035	2.49		7.4
(CO_2 Sat'd. H_2O)	0.020	2.42		5.6
10 - HCO_3^- 5 - Cl^-	0.019	2.00	8.0	7.8
50 - HCO_3^- 5 - Cl^-	0.037	1.42	7.6	7.8**
100 - HCO_3^- 5 - Cl^-	0.064	1.20	8.0	7.7
10 - H_2O_2	0.018	1.96		6.8
100 - H_2O_2	0.015	1.67		7.4
10 - H_2O_2 5 - Cl^-	0.015	3.05		7.4
10 - H_2O_2 100 - Cl^-	0.013	2.68		7.4
100 - H_2O_2 5 - Cl^-	0.015	2.73		7.4
100 - H_2O_2 100 - Cl^-	0.012	2.08		7.3
10 - H_2O_2 10 - HCO_3^- 5 - Cl^-	0.017	2.07		7.7

* See page 27.

** See page 27.

TABLE V (contd.)

Solution (ppm)	Average Penetration (mils/308 hours)	Avg. Film Wt. Avg. Wt. Loss	Initial pH	Hot pH
10 - H ₂ O ₂ } 100 - HCO ₃ ⁻ } 5 - Cl ⁻ }	0.064	1.37		8.3
10 - H ₂ O ₂ } 10 - HCO ₃ ⁻ }	0.018	1.71		7.9
100 - H ₂ O ₂ } 10 - HCO ₃ ⁻ }	0.024	1.55		7.8
10 - H ₂ O ₂ } 100 - HCO ₃ ⁻ }	0.071	1.20		8.3
100 - H ₂ O ₂ } 100 - HCO ₃ ⁻ }	0.073	1.19		8.2
100 - NO ₃ ⁻	0.014	2.56		7.2
100 - NO ₃ ⁻ } 100 - HCO ₃ ⁻ }	0.063	1.29		8.2
100 - NO ₃ ⁻ } 5 - Cl ⁻ }	0.016	2.52		6.7
100 - SO ₄	0.013	2.61		7.0
100 - SO ₄ ⁼ } 100 - HCO ₃ ⁻ }	0.079	1.42		8.3
100 - SO ₄ ⁼ } 5 - Cl ⁻ }	0.012	2.57		6.8
100 - Cl ⁻ } 100 - HCO ₃ ⁻ } 100 - H ₂ O ₂ } 100 - NO ₃ ⁻ } 100 - SO ₄ ⁼ }	0.062	1.28		8.6
100 - SiO ₃	0.026	0.45	8.2	7.4
100 - SiO ₃	1.88	0.12	10.9	9.8
100 - SiO ₃	1.48	0.20	2.2	3.6
100 - SiO ₃	0.069	0.39	3.5	4.4
2 - Cr ₂ O ₇ ⁼	0.011	1.73	7.1	6.7
2 - Cr ₂ O ₇ ⁼	0.006	0.72	6.0	5.6
2 - Cr ₂ O ₇ ⁼	0.006	0.96	5.0	5.3
2 - Cr ₂ O ₇ ⁼	0.006	1.08	4.0	4.5

TABLE V (contd.)

Solution (ppm)	Average Penetration (mils/308 hours)	Avg. Film Wt. Avg. Wt. Loss	Initial pH	Hot pH
100 - Acetate	0.022	2.23	6.3	7.2*
100 - Acetate	0.014	2.02	4.0	4.5
100 - Oxalate	0.033	1.95	6.3	7.4*
100 - Oxalate	0.576	0.51	3.1	4.1
100 - Citrate	0.201	0.78	7.2	7.9*
100 - Citrate	0.464	0.11	3.6	4.4
100 - AsO_4^{3-}	0.117	0.64	7.7	7.9*
10 - $\text{Mo}_7\text{O}_{24}^{6-}$	0.006	2.17	4.3	5.0
10 - $\text{Mo}_7\text{O}_{24}^{6-}$	0.008	1.97	4.7	5.3
100 - $\text{Mo}_7\text{O}_{24}^{6-}$	0.018	0.77	4.2	4.7
100 - $\text{Mo}_7\text{O}_{24}^{6-}$	0.002	1.22	4.5	5.1
100 - PO_4^{3-}	0.023	0.61	7.0	7.7*
100 - PO_4^{3-}	0.040	0.56	7.6	7.9*
100 - PO_4^{3-}	0.164	0.55	8.5	8.5
100 - PO_4^{3-}	0.002	1.89	5.5	6.1
100 - PO_4^{3-}	0.000		5.3	6.6
100 - PO_4^{3-}	0.007	0.64	3.3	3.9
100 - PO_4^{3-}	0.001	0.00	3.6	4.3
10 - PO_4^{3-}	0.000		6.0	6.4*
1 - PO_4^{3-}	0.004	0.71	6.0	6.8*
0.1 - PO_4^{3-}	0.010	2.33	5.9	6.5*
0.01 - PO_4^{3-}	0.005	2.57	6.3	6.6*
100 - Cl^-	0.173	0.49		8.4
100 - HCO_3^-				
100 - H_2O_2				
100 - NO_3^-				
100 - SO_4^{2-}				
100 - PO_4^{3-}				
100 - Cl^-	0.032	0.66		8.3
100 - HCO_3^-				
100 - H_2O_2				
100 - NO_3^-				
100 - SO_4^{2-}				
100 - PO_4^{3-}				

* See page 27.

TABLE V (contd.)

Solution (ppm)		Average Penetration (mils/308 hours)	Avg. Film Wt. Avg. Wt. Loss	Initial pH	Hot pH
100 -	Cl ⁻	0.050	0.63	6.8	8.0**
	HCO ₃ ⁻				
	H ₂ O ₂				
	NO ₃ ⁻				
	SO ₄ ⁼				
	PO ₄ ⁼				
	SiO ₃				
Tap Water	Tap Water (Table III)	0.083	0.67	7.6	8.1**
	100 - PO ₄ ⁼	0.015	1.33	7.0	8.1**
	10 - PO ₄ ⁼	0.050	0.99	7.7	8.2**
	1 - PO ₄ ⁼	0.081	0.77	7.4	7.8**
Reactor Process Water	Reactor Process Water (Table IV)	0.070	0.85	7.1	7.5**
		0.048	1.08	7.0	8.0**
		0.064	0.95	7.0	7.9**
		0.075	0.79	7.3	8.0**
		0.076	0.88	7.3	8.0**
		0.046	0.82	7.0	7.8**
		0.006	0.48	6.0	7.7**
		0.003	1.23	5.0	6.9
		0.004	1.00	4.0	4.7
	1 - PO ₄ ⁼	0.027	1.88	7.0	8.1**
	2 - PO ₄ ⁼	0.002	2.00	7.0	8.1**
	3 - PO ₄ ⁼	0.004	2.00	7.0	8.0**
	4 - PO ₄ ⁼	0.002	2.80	7.0	8.1**
	5 - PO ₄ ⁼	0.005	1.64	7.0	8.0**
	1 - PO ₄ ⁼	0.004	0.27	6.0	7.2**
	1 - PO ₄ ⁼	0.002	0.33	5.0	6.5
	1 - PO ₄ ⁼	0.003	1.00	4.0	4.6
	0.5 - PO ₄ ⁼	0.077	0.85	7.1	8.0**
	1.0 - PO ₄ ⁼	0.067	0.81	7.0	8.0**
	2.0 - PO ₄ ⁼	0.043	0.80	7.0	8.0**
	5.0 - PO ₄ ⁼	0.007	1.93	7.1	8.0**
	10.0 - PO ₄ ⁼	0.006	1.59	6.9	8.0**
	30.0 - PO ₄ ⁼	0.003	0.67	6.5	7.7**
	100 - PO ₄ ⁼	0.001		4.0	4.3
Citrate-Phosphate Buffers		0.210	0.02	4.4	5.4
		0.274	0.14	5.6	6.8
		0.141	0.35	6.0	7.3*
		0.193	0.47	6.5	7.4*
		0.079	0.48	7.4	8.0*

* See page 27.

** See page 27.

c. Dichromate - Phosphate Systems

Aluminum coupons were exposed to solutions containing dichromate ions (0, 0.5, 2.0 and 10 ppm) and phosphate ions (0, 0.5, 2.0 and 10 ppm) at pH 4, 5, 6 and 7 (initial pH). The results are shown in Figures 12 and 13, and the data are given in Table VI. The best correlation of the data is obtained by using the hot pH (Figure 13). This would be expected from the previous discussions. However, since the initial pH gave a more symmetrical set of experiments, they were used for a statistical analysis of variance of the systems. The analysis of variance showed that pH was a significant variable and that there was a significant phosphate-dichromate interaction. That is, the effect of phosphate was dependent on the dichromate concentration and vice versa. In both cases, significance was found at the 99 per cent confidence limit. Examination of Figure 13, in which the hot pH was used to correlate the data, shows an effect of pH in all cases except when 10 ppm of dichromate is present. This observation that dichromate reduces the effect of pH is in agreement with earlier work reported by Lutton.⁽³⁶⁾ Figure 13 also shows that phosphate inhibits uniform corrosion except in the presence of 10 ppm dichromate. This inhibition is the phosphate-dichromate interaction shown by the previously mentioned analysis of variance.

The statistical treatment of these data was performed by C. Groot and W. Nicholson.

d. Extended Exposure Tests

To determine the effect of exposure time on the uniform corrosion, six tests were run for a total exposure of 1025 hours. Two tests each were run in an inhibited system (100 ppm phosphate), an enhanced system (100 ppm citrate), and distilled water. The results are shown in Figures 14 and 15 and the data are given in Table VII. In the distilled water and in the phosphate solution, the corrosion process was complete by the first sampling period, 163 hours, and no additional corrosion took place up to 1025 hours. The

FIGURE 12

CORROSION IN DICHROMATE - PHOSPHATE SYSTEMS

FIGURE 13

CORROSION IN DICHROMATE - PHOSPHATE SYSTEMS

TABLE VIDICHROMATE-PHOSPHATE INHIBITOR DATA

<u>Dichromate (ppm)</u>	<u>Phosphate (ppm)</u>	<u>Average Penetration (mils/308 hours)</u>	<u>Initial pH</u>	<u>Hot pH</u>
0.0	0.0	0.013	7.0	7.0
0.0	0.0	0.009	6.1	6.4 *
0.0	0.0	0.005	5.1	5.9
0.0	0.0	0.002	4.0	4.8
0.0	0.5	0.004	7.0	5.9
0.0	0.5	0.003	6.0	5.5
0.0	0.5	0.001	5.0	5.1
0.0	0.5	0.002	4.0	4.5
0.0	2.0	0.004	7.0	6.2
0.0	2.0	0.004	6.0	5.9
0.0	2.0	0.002	5.0	5.3
0.0	2.0	0.001	4.0	4.6
0.0	10.0	0.007	7.0	6.1
0.0	10.0	0.002	6.0	5.9
0.0	10.0	0.002	5.0	5.0
0.0	10.0	0.001	4.0	4.8
0.5	0.0	0.010	7.0	6.8
0.5	0.0	0.010	6.0	6.8 *
0.5	0.0	0.004	5.0	5.3
0.5	0.0	0.005	4.0	4.8
0.5	0.5	0.005	7.0	6.7
0.5	0.5	0.001	5.9	5.6
0.5	0.5	0.003	4.9	5.2
0.5	0.5	0.003	4.0	4.5
0.5	2.0	0.006	7.1	6.2
0.5	2.0	0.000	6.0	5.5
0.5	2.0	0.006	5.0	5.3
0.5	2.0	0.005	4.0	4.6
0.5	10.0	0.011	6.9	6.8
0.5	10.0	0.001	6.0	6.2 *
0.5	10.0	0.001	5.0	5.6
0.5	10.0	0.001	4.0	4.4

* See page 27.

TABLE VI (contd.)

<u>Dichromate (ppm)</u>	<u>Phosphate (ppm)</u>	<u>Average Penetration (mils/308 hours)</u>	<u>Initial pH</u>	<u>Hot pH</u>
2.0	0.0	0.012	7.1	6.7
2.0	0.0	0.006	6.0	5.6
2.0	0.0	0.006	5.0	5.3
2.0	0.0	0.006	4.0	4.5
2.0	0.5	0.008	7.0	6.5
2.0	0.5	0.004	5.9	5.7
2.0	0.5	0.003	5.0	5.4
2.0	0.5	0.005	4.1	4.7
2.0	2.0	0.005	7.0	5.8
2.0	2.0	0.004	6.0	5.9
2.0	2.0	0.005	5.0	4.9 *
2.0	2.0	0.008	4.0	4.6
2.0	10.0	0.007	7.1	6.2
2.0	10.0	0.004	6.0	5.6
2.0	10.0	0.004	5.1	4.8 *
2.0	10.0	0.004	4.0	4.6
10.0	0.0	0.003	7.0	6.9
10.0	0.0	0.002	6.1	6.1
10.0	0.0	0.002	4.9	5.1
10.0	0.0	0.002	4.0	4.8
10.0	0.5	0.005	7.0	6.1
10.0	0.5	0.003	5.9	6.1 *
10.0	0.5	0.004	5.0	5.3
10.0	0.5	0.002	4.0	4.7
10.0	2.0	0.007	7.1	6.8
10.0	2.0	0.006	6.0	6.2 *
10.0	2.0	0.005	5.0	5.5
10.0	2.0	0.003	4.0	4.6
10.0	10.0	0.008	7.0	6.8
10.0	10.0	0.004	6.0	6.2 *
10.0	10.0	0.007	5.0	5.6
10.0	10.0	0.006	4.0	4.7

* See page 27.

FIGURE 14

CORROSION AS A FUNCTION OF TIME

FIGURE 15

CORROSION AS A FUNCTION OF TIME

TABLE VII
EXTENDED EXPOSURE DATA

<u>Solution (ppm)</u>	<u>Penetration (mils)</u>	<u>Time (hours)</u>	<u>Initial pH</u>	<u>Hot pH</u>
100 - Phosphate	0.001	163	5.0	5.6
	0.002	308		5.6
	0.004	309		
	- 0.001	716		3.8
	0.003	717		
	0.002	862		
	- 0.001	1025		3.7
100 - Phosphate	0.003	163	5.0	5.6
	0.001	308		5.6
	0.000	309		
	0.003	716		3.9
	0.005	717		
	0.000	862		
	0.000	1025		3.7
100 - Citrate	0.267	163	3.5	4.4
	0.295	308		4.4
	0.292	309		
	0.657	716		4.4
	0.732	717		
	1.160	862		
	1.410	1025		4.3
100 - Citrate	0.323	163	3.4	4.6
	0.326	308		4.5
	0.455	309		
	0.904	716		4.6
	0.600	717		
	0.604	862		
	1.085	1025		4.4
Distilled Water	0.011	163	5.8	5.6
	0.011	308		5.5
	0.006	309		
	0.009	716		5.6
	0.010	717		
	0.009	862		
	0.010	1025		5.5
Distilled Water	0.010	163	5.8	5.5
	0.011	308		5.4
	0.005	309		
	0.007	716		5.4
	0.007	717		
	0.005	862		
	0.005	1025		5.3

corrosion enhancing effect of the citrate solution is clearly shown. The corrosion process appeared to have reached a steady state during the first 163 hours of exposure and then continued at a fairly rapid rate for the remainder of the 1025-hour exposure. These results support the assumption that the relative corrosion occurring during the first two weeks of exposure at 92° C is indicative of the relative corrosiveness of the solutions.

e. Effect of Flow Rate and Aluminum Ion Concentration

The flow rate was difficult to control in a test in which reactor process water was the corroding medium. Two experiments were involved; one with a glass wool line filter and one without. In the absence of the line filter, foreign matter in the reactor process water plugged the microflow regulator and caused a marked restriction of the flow rate. The results of this test are given as Experiment 1 in Table VIII.

When the flow was less than normal, the corrosion rate was only about a third of that with normal flow. It was surprising to find an effect of solution flow rate at such low flow rates. It is unlikely that the effect was caused by differences in the velocity of the solutions past the aluminum samples since the velocity was so nearly zero in both cases. Even more surprising was the fact that the hot pH in the solution with the restricted flow rate was 8.9, compared to pH 7.9 in the solution with normal flow, and yet the corrosion at the higher pH was less than at the lower pH. This observation was entirely contrary to the previous observations that the corrosion at pH 8.9 should have been much greater than at pH 7.9 as shown in Figure 9.

To determine whether the observed effect was caused by the restricted flow rate or by the absence of the line filter, the test was repeated with carefully controlled normal flow rates in both solutions. The results (Experiment 2, Table VIII) showed that the corrosion was essentially the same in both cases and the previously observed effect must have been caused by restriction of the flow rate. The test was repeated twice again with reactor process water at normal and restricted low flow and twice with

distilled water at normal and restricted low flow. Line filters were used in all experiments and the results are given as Experiments 3, 4, 5, and 6 of Table VIII. When reactor process water was used, low flow and a higher than "normal" hot pH resulted in diminished corrosion (Experiment 3), while low flow and a "normal" hot pH resulted in a lesser decrease in corrosion (Experiment 4). The observation that the hot pH was higher in the cases of restricted low flow is probably caused by the increased residence time of the solutions in the corrosion cells resulting in a greater liberation of CO_2 . When distilled water was used, the hot pH did not exceed 7.1 and no effect of flow rate was observed (Experiments 5 and 6).

At the conclusion of Experiments 3 and 5, the solutions contained in the corrosion cells were analyzed for their aluminum content by emission spectroscopy. Aluminum concentrations of reactor process water at normal flow and of distilled water at normal and low flow were 0.036, 0.039, and 0.037 parts per million respectively. Reactor process water at low flow with a high hot pH contained 0.235 ppm of aluminum. Therefore the corrosion inhibition was probably caused by the buildup of a relatively high concentration of aluminate ions in the more basic solution as a result of the decreased flow rate and the higher pH.

To test this conclusion, Experiments 7, 8, and 9 were run with solutions of aluminum salts in distilled water at normal flow rates. In Experiment 7, aluminum sulfate was added to give 10 ppm aluminum and the pH was adjusted to 7.0 with NaOH. In Experiment 8, aluminum nitrate was used. In both experiments the aluminum precipitated as the hydroxide, leaving the aluminum concentrations at 0.026 ppm and 0.040 ppm respectively. No reduction of corrosion was observed in either of these cases. In Experiment 9, about 10 ppm of Aluminum was added as aluminum nitrate and the pH was adjusted to 9.0 with NaOH. As the NaOH was added, the aluminum first precipitated and then redissolved, presumably as aluminate ions. Analysis of the solution showed an actual concentration of 6.1 ppm of aluminum. The observed corrosion in this case was about one-fifth of the amount which would be predicted from Figure 9 at pH 8.7 (although it was more than would

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TABLE VIII

EFFECT OF FLOW RATE AND ALUMINUM ION CONCENTRATION

Exp't	Solution	Flow Rate	Penetration (mils/308 hours)	Initial pH	Hot pH	Remarks
1	Reactor Process Water	Normal	0.064	7.0	7.9	No line filter
	Reactor Process Water	Low	0.023	7.0	8.9	
2	Reactor Process Water	Normal	0.075	7.3	8.0	No line filter
	Reactor Process Water	Normal	0.052	7.3	8.0	
3	Reactor Process Water	Normal	0.076	7.3	8.0	Final Al { 0.036 ppm Analysis { 0.235 ppm
	Reactor Process Water	Low	0.024	7.3	8.4	
4	Reactor Process Water	Normal	0.046	7.0	7.8	
	Reactor Process Water	Low	0.034	7.0	7.9	
5	Distilled Water	Normal	0.011	5.4	6.9	Final Al { 0.039 ppm Analysis { 0.037 ppm
	Distilled Water	Low	0.009	5.4	5.0	
6	Distilled Water	Normal	0.012	5.4	7.1	
	Distilled Water	Low	0.014	5.4	4.9	
7	10 ppm Al ($\text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ in process H_2O) Initial analysis of settled solution = 0.026 ppm Al	Normal	0.044	7.0	7.4	Solution initially adjusted to pH 7 with NaOH.
8	10 ppm Al ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in process H_2O) Initial analysis of settled solution = 0.040 ppm Al	Normal	0.036	7.0	7.8	Solution initially adjusted to pH 7 with NaOH.
9	10 ppm Al ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in Dist. H_2O) Initial analysis of solution = 6.1 ppm Al	Normal	0.046	9.0	8.7	Solution initially adjusted to pH 9 with NaOH.

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be predicted at pH 6). This result confirms the previous conclusion that a high concentration of aluminate ions inhibits aluminum corrosion in basic solutions.

f. The pH of Minimum Corrosion at Elevated Temperatures

Samples of 1245 aluminum were exposed to 0.2 M acetate buffer solutions at temperatures up to 300° C. The results are shown in Figure 16 and in Table IX. At the conclusion of 300° C test, the pH of the pH 3.1 and pH 4.0 buffers was measured at room temperature. The pH of the solutions had increased by 0.2 and 0.1 pH unit, respectively, showing no appreciable effect of heating on the room temperature pH of the buffers. At 300° C and 280° C, minimum corrosion occurred at pH 3.1. At pH 6.0, 6.6, and 7.9, the samples were completely destroyed by intergranular penetration corrosion. At 255° C, the minimum corrosion occurred at pH 4.0. At 205° C, the minimum corrosion occurred at pH 4.9.

To eliminate the occurrence of intergranular penetration corrosion, these tests were repeated using M388 aluminum, (1% Ni, 0.5% Fe, 0.1% Si, balance Al) which is noted for its resistance to intergranular penetration corrosion at elevated temperatures. The results are shown in Figure 17 and in Table X. A smaller range of pH was covered in these tests in order to provide experimental points that were closer together. At 305° C and 255° C, the pH of minimum corrosion appeared to be at pH 3.1 or less. At 210° C, the minimum corrosion occurred at pH 4.9. This is in agreement with the data for alloy 1245 at 205° C as shown in Figure 16.

FIGURE 16

CORROSION OF 1245 ALUMINUM AT ELEVATED TEMPERATURES

FIGURE 17

CORROSION OF M-388 ALUMINUM AT ELEVATED TEMPERATURES

TABLE IXCORROSION DATA FOR 1245 ALUMINUM AT ELEVATED TEMPERATURES

	pH					
	<u>3.1</u>	<u>4.0</u>	<u>4.9</u>	<u>6.0</u>	<u>6.6</u>	<u>7.9</u>
300° C-18 hours	0.17*	0.20	9.84	-----Destroyed----- -----Intergranular Attack-----		
280° C-26 hours	0.11	0.12	0.46	-----Destroyed----- Intergranular Attack----		
255° C-70 hours	0.24	0.12	0.15	1.08	1.81	2.60
				Intergranular Attack		
205° C-117 hours	0.12	0.11	0.06	0.15	0.23	0.54

* Numbers in body of table are mils penetration

TABLE XCORROSION DATA FOR M388 ALUMINUM AT ELEVATED TEMPERATURES

	pH						
	<u>3.1</u>	<u>3.5</u>	<u>4.0</u>	<u>4.5</u>	<u>4.9</u>	<u>5.5</u>	<u>6.0</u>
305° C-115 hours	0.35*	0.50	0.55	0.71	1.63	3.44	
255° C-87 hours	0.26	0.28	0.30	0.33	0.32	0.45	
210° C-115 hours	0.13	0.16	0.12		0.12	0.15	0.25

* Numbers in body of table are mils penetration

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