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AE
AP Memo No. 44

CORROSION OF FUEL ELEMENT MATERIALS

FOR A

LOW ENRICHMENT POWER REACTOR

Contract No. DA-44-009 Eng. 2868

Issued August 1, 1956

CLASSIFICATION CANCELLED
DATE 7-3-57
For The Atomic Energy Commission

H. F. Canale
Chief, Declassification Branch *fu*

Alco Products, Inc.
Post Office Box 414
Schenectady, New York

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Issued August 1, 1956

By

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ABSTRACT

To determine their possible use as fuel element material, an evaluation was made of the corrosion characteristics of aluminum, zirconium, stainless steel and their alloys. The corrosion behavior of these metals under conditions that would prevail in a low enriched water cooled and moderated reactor of the APPR is as follows:

- (1) Zircaloy-2 and 3 are more suitable for reactor application than crystal bar zirconium. The average corrosion rate for Zircaloy-2 in 500 F water is $0.05 \text{ mg/cm}^2/\text{mo}$.
- (2) Stainless steel was the most corrosion resistant material investigated; its corrosion rate in 500 F water averages $.04 \text{ mg/cm}^2/\text{mo}$.
- (3) Commercial 2S aluminum is unsatisfactory above 400 F. However, when alloyed with nickel or copper, or plated with nickel, corrosion rates are significantly reduced. In 500 F water (pH-7) the corrosion rate of aluminum - 1% nickel and aluminum - 6% copper alloys is approximately $0.9 \text{ mg/cm}^2/\text{mo}$ (1.5 mils/yr) at a flow rate of 6 fps.
- (4) Generally, corrosion rates of all these metals vary considerably with changes in temperature, flow rate, pH and other conditions.

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INTRODUCTION

In the past several years an increasing demand has occurred for metals which can withstand the corrosive effects of a high temperature aqueous medium. In reactors where temperature conditions are quite variable, three metals have been primarily used as core and clad material for fuel elements, namely aluminum, zirconium, stainless steel or alloys of either aluminum or zirconium.

Under a study for a low enriched reactor of the APPR type, in which water is used both as a coolant and moderator, an evaluation of the corrosion behavior of these three metals was made to determine their applicability at temperatures of 400 - 600 F.

The literature was reviewed and personal contacts were held with men engaged in current material testing to determine the corrosion rates of these above materials.

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SECTION I

ALUMINUM AND ALLOYS OF ALUMINUM

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I - HIGH PURITY ALUMINUM

In ordinary low temperature applications, the corrosion rate decreases with increasing aluminum purity. When exposed to aqueous mediums at elevated temperatures, high purity aluminum is not as satisfactory as several commercial aluminum alloys. Lavigne⁽¹⁾ reports that 99.99% aluminum corrodes intergranularly in both 300° F. and 212° F. distilled water at a pH of 5.0-7.0. Microexamination of the corroded specimens revealed that the attack took place preferentially at the boundaries of contiguous grains having different orientations. At 300° F. sometimes the attack did not occur in unannealed high purity aluminum but always occurred in the annealed condition.

Lavigne concluded that metallurgical factors such as the texture have great bearing on the corrosion resistance of high purity aluminum. In tests conducted in distilled water at 300° F. high purity aluminum having 0.1% Si, either annealed or unannealed, did not suffer intergranular attack.⁽²⁾

Samples cold-worked from 5 to 50% inclusive and all samples annealed sufficiently to complete recrystallization corroded intergranularly in distilled water at 212° F.⁽³⁾ Unannealed materials cold-worked to 60% and over were immune against this attack. From 300° F. to 400° F., the 60 and 70% cold-worked materials corroded intergranularly while those cold-worked 80 and 90% corroded generally. At temperatures above 400° F., cold-working did not render the material immune to intergranular

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corrosion. At temperatures above or below 400° F. annealing until complete recrystallization occurs, such as 750° F. for 1 hour, sensitizes the material, rendering it susceptible to intergranular corrosion.

Based on short time static tests in distilled water at 400° F. the best corrosion rate was obtained using 90% cold-worked 99.99% aluminum. This rate was 528 mils/yr penetration. From these and other results, the use of high purity aluminum for high temperature reactor applications is not deemed likely.

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II - COMMERCIAL 2S ALUMINUM

Commercial 2S, now known as 1100 aluminum in the four digit system*, is commercially pure aluminum** having the following nominal composition:

Aluminum	99.5 %
Copper	0.005%
Iron	0.004%
Silicon	0.004%
Others	0.15 % max.

In water containing low solid concentrations, the corrosion rate of 2S aluminum increases with increasing temperatures. The rate is initially relatively rapid but declines with time, changing from about 0.05 to 1.3 mils/yr average penetration rate as the temperature increases from 250° F. to 400° F. The change in this range is linear. Above 400° F. intergranular attack occurs, with resultant more rapid penetration. (4)

* The four digit designation system for commercial aluminum alloys is listed in Table I of Appendix.

** Specifications for materials evaluated are listed in Table II of Appendix.

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A. MECHANISM OF CORROSION

Microscopic examination has shown that the corrosion product formed on 2S aluminum in relatively pure water characteristically takes the form of a two-layered film.⁽⁴⁾ The inner layer is thin and is probably less than several tenths of a micron thick. This layer is quite protective with its crystal orientation perhaps being determined by the base metal crystal orientation. Corrosion proceeds through this layer of film, or more likely, through imperfections in it. If the film is stripped from the metal surface, the latter is characteristically pock-marked or etched in appearance. This non-uniform nature of attack is correlated to microscopically revealed breaks in the film. During corrosion the thickness of inner film builds up for the initial reaction period, then apparently remains constant, indicating that the inner layer controls the corrosion reaction.

As this film is formed, it continuously breaks loose or recrystallizes to form the much thicker white or gray corrosion product layer on the outside. This outer layer appears porous and apparently does not control the rate of corrosion, since the rate does not change as the layer grows thicker. As does the inner film, the outer layer initially builds up rapidly and then levels off, as illustrated in Figure 1 for 2S aluminum in oxygen-saturated, distilled water at 120° F. At this temperature the curves show more clearly the leveling off of corrosion with time. Small changes in weights make it extremely difficult to interpret data to ± 0.01 MDD ($\text{mg}/\text{dm}^2/\text{day}$).

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Figure 1

CORROSION OF 2S ALUMINUM IN OXYGEN-SATURATED DISTILLED WATER AT 120°F

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The corrosion rate of 2S aluminum in distilled water increases with temperature. At about 212° F. there is a sharp break in the plot of corrosion rate versus temperature. The reasons for this phenomenon are not well understood, but it is apparently related to the change in stable corrosion product occurring near this temperature. The change in corrosion rate as a function of temperature follows an Arrhenius plot at temperatures of 250 F. to 400 F., indicating an unchanging corrosion mechanism in this range.

Above 400° F. a transition in the corrosion behavior of 2S aluminum takes place. It first develops a smooth adherent coating of α $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ as it does below 400° F., but with increasing test time or temperature the surface of the oxide begins to roughen. Under the microscope the roughening can be attributed to numerous tiny protuberances emerging from the metal surface. With still further increases in time or temperature, these protuberances grow into mounds that are clearly visible to the naked eye. They form first and most profusely at imperfections in the metal lattice, such as at grain boundaries and stringers. By probing these mounds, a mixture of both oxide and metal is found.

As would be expected, the test conditions necessary for the mounds to become visible and their further rate of growth are also dependent on the metal surface condition. Fine-grained material and less severely distorted structures usually are most resistant to this "blistering" attack. Relatively thin cold-rolled sheet is most susceptible, with the attack becoming even more severe if the material is given a grain

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coarsening anneal which is believed to result in grain boundary thickening. Extruded bars are generally more resistant, which may account for the improved corrosion resistance effected by Lavigne⁽³⁾ in experiments by carefully rolled high purity aluminum. This process probably resulted in surface grain orientation and compacting.

Onset for this blistering varies from a few weeks at 480° F. to a few hours at 600° F. for annealed sheet stock. The corrosion rate (slope of the weight change versus time curve) begins to rise rapidly at an accelerating rate as attack commences. As a consequence, penetration of the metal occurs at the most active locations resulting in localized disintegration of the material.

B. CORROSION PRODUCT

The primary corrosion products of aluminum can be expressed as $Al_2O_3 \cdot XH_2O$. To determine the value of X, Draley and Ruther⁽⁴⁾ calculated it for the corrosion product of 2S aluminum as shown in Table I. In their calculations, it was assumed that no corrosion products were lost from the sample surface during the tests. Values of X less than 1 in Table I can be presumed to mean that some of the corrosion product has been lost to the solution.

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TABLE I
VALUES OF X IN FORMULA $Al_2O_3 \cdot xH_2O$

Temperature ($^{\circ}F$)	pH 5.0	pH 7.0	pH 8.5
212	1.2	1.3*	1.0
250	1.2	1.1	0.52
300	0.94	0.65	0.62*
350	1.0	0.65	0.19
400	1.2*	0.50	0.12

* X-ray diffraction

As the temperature is increased the pH must be increasingly more acidic to prevent dissolution of the corrosion product. Perhaps this is due to the increase in hydroxide ion concentration in the solution resulting from the liberation of hydrogen gas.

X-ray diffraction studies showed that the corrosion product indicated by asterisks in Table I was α $Al_2O_3 \cdot H_2O$. This may explain the discontinuity in the plot of corrosion rate versus temperature as shown in Figure 2 where the sharp break in the curve occurs at about $212^{\circ} F$. Below this temperature, X-ray diffraction reveals the relatively thick corrosion product to be β $Al_2O_3 \cdot 3H_2O$. The temperature at which this transition in the bulk corrosion product takes place also seems to be a function of the solution composition but is approximately $200-212^{\circ} F$.

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Figure 2

CORROSION RATE FOR 2S ALUMINUM FROM 50 - 275°C

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Whether or not this transformation is pertinent to the break in the curve is not certain since the thin film of undetermined structure and not the relatively thick corrosion product controls corrosion rate.

Dummy and active assemblies removed from the Bulk Shielding Reactor were pitted and corroded.⁽⁵⁾ The dummy assembly was made of 2S aluminum while the active elements were clad with 2S having an outer cladding of 72S aluminum. (72S is similar in composition to 2S except it has a nominal 1% zinc). Corroded areas were covered with a heavy white eruption of corrosion products and a typical analytical result for the composition of these deposits is given in Table II. The high silicon content is due to the Al-Si brazing alloy which was the most severely attacked material.

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TABLE II
IDENTIFICATION OF CORROSION PRODUCTS
REMOVED FROM DUMMY FUEL ASSEMBLY

X-ray Diffraction: No specific diffraction pattern found.

Spectrographic Analysis:

Element	Percent	Element	Percent
Al	5 or more	Ni	less than 0.05
Ba	less than 0.02	Pb	less than 0.05
Co	less than 0.05	Si	2.0
Cr	0.1	Sn	less than 0.02
Cu	0.02	Ti	less than 0.01
Fe	0.1	U	less than 1.0
Mg	0.05	V	less than 0.02
Mn	less than 0.01	Ar	less than 0.1
Mo	less than 0.02		

Chemical Analysis:

Element	mg/g	Possible Oxide	Percent
Al	246	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	71.0
Cr	0.25	Cr_2O_3	
Fe	1.41	Fe_2O_3	0.2
Si	13.9	SiO_2	3.0
U	0.54	U_3O_8	0.06
Unidentified			25.8

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C. Interrelation of pH and Temperature Effects

The corrosion rate of 2S aluminum in nearly pure water is markedly affected by the pH which in turn is temperature dependent. At all temperatures a pH of minimum corrosion exists which decreases with increasing temperatures. At temperatures below 212° F. the optimum pH is approximately 6.0 to 6.5; at 600° F. this shifts to about 2. Variations from this pH of minimum corrosion generally increase the deleterious effect of other variables such as flow rate. Shifts acid of the pH of minimum attack are less damaging than shifts alkaline. This is illustrated by the observation that at all temperatures above 212° F. the corrosion rate is less in dilute sulfuric and nitric acid solutions than in neutral water. In addition the blistering attack can apparently be prevented by the reduced pH's. This progressive improvement is illustrated in Table III where the pH was adjusted from 6 to 2 by the addition of sulfuric acid. At pH 1, apparently acid attack caused areas of local etching.

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TABLE III
CORROSION OF 2S ALUMINUM AT 600° F. *

<u>pH</u>	<u>Sample Weight Change, mg</u>
6.10	800
4.98	450
3.91	7.0
3.07	6.8
2.05	5.7
1.13	-18.9

*After 2 hours in Dilute H_2SO_4

Almost identical results were obtained in nitric acid and presumably other acids would be satisfactory except for those containing halogen ions or other ions which might have a specific effect. In later tests no effect of sulfate or nitrate ion could be shown. Therefore, observed effects are attributed to the hydrogen ion concentration.

On the alkaline side of the optimum pH the rate increases much more rapidly than on the acidic side. Apparently the increased corrosion results from the increasing solubility of the corrosion product at more alkaline pH's. The increase in corrosion rates on the alkaline side is even more profound at high temperatures and higher flow rates. In some instances, reducing the pH from 7.7 to 7.3 will halve the corrosion rate. (6)

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The effect of pH on the corrosion rates of 2S aluminum at 120° F. is shown in Figure 3. The pH of "minimum attack" discussed above is clearly shown in this plot. As stated above, increasing the temperature increases the corrosion rate as shown in Figure 4 and Figure 5. Even at these higher temperatures the optimum pH effect is noted. Table IV summarizes the effect of pH and temperature on corrosion rates.

TABLE IV
INTERRELATION OF pH AND TEMPERATURE EFFECT
ON THE CORROSION OF 2S ALUMINUM

Temperature (°F)	pH	Slope (Corrosion Rate) (mg/cm ² /mo)	Intercept (mg/cm ²)
120	7	.006	.43
212	7	.087 (inaccurately determined)	.21
250	5	.018	.21
	7	.030	.13
	8.5	.174	.27
300	5	.039	.16
	7	.108	.20
	8.5	.261	.27
350	5	.102	.18
	7	.264	.18
	8.5	.390	.37

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Figure 3

EFFECT OF pH ON CORROSION OF 2S ALUMINUM
IN OXYGEN SATURATED WATER AT 120F

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Figure 4

CORROSION OF 2S ALUMINUM AS A FUNCTION OF pH

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Figure 5

CORROSION OF 2S ALUMINUM FROM 200F TO 550F

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TABLE IV - Cont.

Temperature (°F)	pH	Slope (Corrosion Rate) (mg/cm ² /mo)	Intercept (mg/cm ²)
400	5	.240	.58*
	7	.750	.54
	8.5	2.28 (6 to 17 days)	.25
525	7	7.20	.64

* Apparently an accident during test.

D. EFFECT OF INHIBITORS

At temperatures around 120° F. the corrosion rate of 2S aluminum in pure water is reduced by the additions of oxidizing agents such as dissolved oxygen or dilute dichromate. The corrosion rate has also been reduced by additions of soluble silica. Dichromate, in particular, has long been recognized as an effective corrosion inhibitor for aluminum systems at temperatures below 130° F. The ion inhibiting corrosion at slightly alkaline pH's is the chromate ion ($\text{CrO}_4^{=}$) since dichromate only exists in slightly acidic solutions.

Halas⁽⁷⁾ conducted experiments to see if the chromate ion was effective when present in the range of only a few parts per million. Previously, low concentrations of chromate ion were considered both detrimental and beneficial in preventing accelerated pitting of aluminum.

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Under test conditions listed in Table V, sodium dichromate was found effective as an inhibitor in concentrations as low as 0.1 ppm. Intermittent additions of chromate in the water, or pretreatment of the aluminum with chromate, provides limited inhibition if the environment to which the metal is exposed is capable of only slowly damaging the oxide film.

TABLE V
COMPOSITION OF TEST WATER
(Concentrations in ppm)

	<u>Average</u>
pH (measured at ambient water temperature)	7.65
Methyl Orange Alkalinity (as ppm of CaCO ₃)	54.
Fe	0.010
Ca	21
Mg	4.7
Cu	0.007
Al	0.07
Chloride Ion	1.5
Sulfate Ion	17
Suspended Solids	less than 0.2
Specific Resistance (measured at 77°F.)	6100 ohm-cm

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Experiments were conducted using radioactive chromium to investigate the mechanism by which dichromate protects aluminum. Coupons of 2S aluminum were exposed to a recirculating $\text{Cr}^{51}\text{O}_4^-$ solution, and the activity picked up counted to determine the rate of chromium adsorption. The coupons were subsequently placed in a stream of cold water flowing with a velocity of about 1 fps and at a temperature of about 60° F. This water had the same composition as shown in Table V. The change of activity before and after washing was used to calculate the amount of chromium removed by washing from the aluminum surface. Radioautographs were taken of some of the radioactive coupons to determine the distribution of the chromium. Since activity of the stock solution was determined, an estimate could be made of the actual amount of chromium deposited on the coupons.

From these experiments Halas proposed that with dichromate a chemical reaction with the aluminum surface occurs followed by the inclusion of chromic oxide in the aluminum oxide. This reaction results in the formation of a non-porous, defect-free oxide.

Arguments for chemical adsorption (vs. physical adsorption), that is for the chromate to be reduced on the Al surface and then become included in the aluminum oxide, are listed below. An action of this type may result in corrosion inhibition by virtue of creating a more tenacious aluminum oxide.

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1. The chromium adsorbed is a function of the amount of corrosion that has taken place since the chromium adsorbed per unit area would be a function of the amount of oxide present on the area in question.
2. Adsorption of dichromate on aluminum is apparently irreversible-chemical adsorptions are usually irreversible.
3. Erosion-corrosion is halted by 1 ppm sodium dichromate. Where suspended solids in the rapidly flowing water have broken the surface of the oxide the rate at which a new protective oxide forms is difficult to attribute to physical adsorption.
4. The amount of chromium adsorbed is a function of temperature. Physical adsorption should be relatively unaffected or even decreased by elevating the temperature.
5. The chromium adsorbed is unable to be desorbed by washing in flowing water.
6. The rate of corrosion is most likely controlled by the rate at which ions can diffuse to and away from the aluminum surface. For any steady state thickness of oxide, the rate of ion diffusion is apparently unaffected by the presence of dichromate. This means that the action of the dichromate is not to set up a diffusion barrier as hypothesized for physical adsorption, but only to strengthen the oxide against defects.

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7. Chemical adsorption considers the inhibitor as being anodic.

Potential measurements have shown that chromate is an anodic inhibitor for aluminum, as well as for other materials.

Based on the beneficial effect of these corrosion inhibitors at low temperatures, potassium dichromate and sodium metasilicate, with and without pH control, were therefore chosen by Ruther (8) as possible high temperature inhibitors for investigation at 400° F. Results of these experiments are shown in Table VI.

TABLE VI
EFFECT OF CORROSION INHIBITORS OF 2S ALUMINUM AT 400° F.

Solution	Gas	Corrosion Rate mg/cm ² /mo	Intercept mg/cm ²
Distilled water pH 6.8	Deaerated	0.75	.54
50 ppm K ₂ Cr ₂ O ₇ pH 6.1 (adjusted with KOH)	Deaerated	0.27	0
50 ppm K ₂ Cr ₂ O ₇ pH 8.4 (KOH)	Deaerated	0.63	0
30 ppm SiO ₂ (added) as Na ₂ SiO ₃ pH 9.4 H ₂ SO ₄	Deaerated	0.30	0
30 ppm SiO ₂ pH 3.6 (H ₂ SO ₄)	Deaerated	0.06	.14

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These results indicate that only a combination of low pH and silica proved beneficial; the other additions actually increased the corrosion rate from 4 to 9 times that obtained in distilled water. At the high rates obtained with neutral and alkaline solutions, the intercept is essentially zero which is a departure from the usual aluminum behavior, indicating that possibly the mechanism of corrosion was different. If one applies Uhlig's theory of passivity, the actual concentrations of these inhibitors may have influenced the results. The use of these common low temperature corrosion inhibitors appears to be unwise at 400° F. unless pH adjustments are also used.

E. EFFECT OF CHLORIDES

Chloride ions produce pitting and increased corrosion of aluminum in aqueous solutions at ordinary temperatures. Studies at the MTR⁽⁹⁾ indicated that as little as 0.5 ppm of chloride in demineralized water can cause severe pitting of aluminum.

Tests were performed with a 5 ppm Cl⁻ solution (KCl) at a pH of 3.5 (helium saturated) to evaluate this tendency at 400° F.⁽⁸⁾ An average of about 1 pit for every three square centimeters was formed on specimens exposed for 19 days. The pits were typically surface channels with a length to breadth ratio of 3 or more and a maximum depth of 0.6 mm. Dimensions of the largest pit was 0.6 mm wide by 2 mm long. The corrosion rate measured for this condition was 1.0 MDD (intercept 18 mg/dm²) as compared to a value of 0.7 MDD

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(intercept 21 mg/dm^2) under similar conditions without the presence of the chloride ion. The effect at 400° F. is apparently somewhat less than at temperatures below 212° F.

F. EFFECT OF ANODIZING

Breden and Monaweck⁽¹⁰⁾ anodized samples of 2S aluminum according to commercial methods followed by a number of post-anodizing treatments prior to testing them in static degassed water at 500° F. The anodizing solutions and corresponding cell operating conditions were as follows with (3) being most effective:

1. 5 wt-% chromic acid at 95° F. and 60 volts.
2. 10 vol-% sulfuric acid at 72° F. and 15 volts.
3. 5 vol-% sulfuric acid at 72° F. and 18 volts.

The most effective post-anodizing treatment consisted of soaking the anodized aluminum in a 0.5 wt % nickel acetate solution at 120° F. for two hours, followed by a two-hour soak either in 5 wt % boiling sodium dichromate solution or boiling water. The lowest corrosion rates at 500° F. were $1.0 \text{ mg/cm}^2/\text{mo}$ for samples post-anodized in dichromate and $2.9 \text{ mg/cm}^2/\text{mo}$ for those boiled in water. From the data it would appear that anodizing is beneficial for the corrosion resistance of 2S aluminum at 500° F.

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G. EFFECT OF ALLOYING ADDITIONS

Based on the corrosion behavior in water below 250° F., numerous investigators report that the addition of alloying elements to pure aluminum decreases its corrosion resistance. Even at 250° F., however, Groot and Peekma⁽⁶⁾ after in-pile testing over 30 alloying additions to aluminum found, as did Lavigne⁽³⁾ that 99.995% and 99.95% aluminum suffered intergranular corrosion.

While alloys may not hold much advantage at very low temperatures, alloying additions such as nickel and copper appear to offer the most promise for reducing the corrosion rate of aluminum exposed to a high temperature aqueous medium.

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III - COMMERCIAL ALUMINUM ALLOYS OTHER THAN 2S

To evaluate the reproducibility of corrosion results obtained in static distilled water at 480° F., multiple samples of pure aluminum (99.0%) were tested for periods up to 572 hours⁽¹¹⁾. For the majority of time intervals, reproducible aluminum corrosion data was obtained. In some tests, the breakdown of the protective film by film eruptions resulted in an accelerated attack on the metal and led to less reproducible data. Good reproducibility of corrosion results will be obtained for systems such as aluminum-water as long as the mode of corrosion is uniform over the surface of the specimens, but when the corrosion is not uniform the results are apt to be questionable.

Dillion, Wilson and Troutner⁽¹²⁾ tested some 50 commercial aluminum alloys in distilled water over the temperature range of 480° F. - 600° F. for periods up to six weeks. As shown in Table VII many of the samples were completely oxidized between observation periods and failure was obvious. In other cases, the samples were rejected for corrosion rates too high to permit useful application of the alloy. In terms of metal penetration, all rejected samples were corroding at rates in excess of 10 mils/mo. Of those samples failing, intergranular attack was evident and the corrosion product frequently contained unreacted aluminum.

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TABLE VII

CORROSION RESISTANCE OF SOME ALUMINUM ALLOYS IN
HIGH TEMPERATURE WATER

Alloy	Per Cent Composition							Time to Failure		
	Cu	Si	Mn	Mg	Zn	Ni	Cr	250 C	300 C	350 C
99.99 Al									1 wk	
99.60 Al								4 wk	2 wk	
2S								6 wk	2 wk	3 hr
2S (As-Cast)										6 hr
M-388(1)						1.0		NF*	NF	NF
99.99 Al 1% Ni						1.0				1 day
3S			1.2					4 wk	2 wk	3 hr
11S(2)	5.5							1 wk	1 wk	6 hr
17S	4.0		0.5	0.5				NF	NF	1 wk
18S	4.0		0.5	0.6		2.0		NF	NF	NF
24S	4.5		0.6	1.5				NF	2 wk	1 wk
25S	4.5	0.8	0.8					NF	2 wk	?
32S	0.9	12.2		1.1		0.9		NF	NF	NF
B50S				1.2				NF	2 wk	3 hr
A51S		1.0		0.6			0.25	6 wk	1 wk	3 hr
52S				2.5			0.25	1 wk	1 wk	3 hr
53S		0.7		1.3			0.25	NF	1 wk	3 hr
A54S				3.5			0.25	3 wk	2 wk	3 hr
56S			0.1	5.2			0.1			3 hr
XK155				0.9				NF*	1 wk	3 hr
XK183			0.75	4.8				1 wk	1 wk	3 hr
XK186			0.5	4.0				1 wk	1 wk	3 hr
61S	0.25	0.6		1.0			0.25	NF	2 wk	3 hr
63S		0.4		0.7				4 wk	1 wk	3 hr
63S / 2% MM**		0.4		0.7				3 wk		3 hr
72S					1.0			4 wk	2 wk	3 hr
75S	1.6			2.5	5.6		0.3	NF	2 wk	3 hr
13		12.0						2 wk	2 wk	1 wk
43		5.0						NF	2 wk	1 wk
85	4.0	5.0						NF	4 wk	2 wk
108	4.0	3.0						NF	4 wk	1 wk
112	7.0				1.7			NF	NF	NF
113	7.0	2.0			1.7			NF	NF	3 hr

* No Failure

** Mischmetal

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TABLE VII(Contd.)

Alloy	Per Cent Composition							Time to Failure		
	Cu	Si	Mn	Mg	Zn	Ni	Cr	250 C	300 C	350 C
122	10.0			0.2				NF	NF	1 wk
Al32	0.8	12.0		1.2		2.5		NF	NF	NF
D132	3.5	9.0		0.8		0.8		NF	NF	2 wk
138	10.0	4.0		0.3				NF	6 wk	2 wk
142	4.0			1.5		2.0		NF	NF	NF
195	4.5	0.8						NF	NF	2 wk
B195	4.5	2.5						NF*	NF	3 hr
212	8.0	1.2						NF	NF	3 hr
214				3.8				1 wk	1 wk	3 hr
A214				3.8	1.8			1 wk	1 wk	3 hr
B214		1.8		3.8				1 wk	1 wk	3 hr
218				8.0				1 wk	1 wk	3 hr
319	3.5	6.3						6 wk	4 wk	2 wk
333	3.8	9.0						NF	NF	NF
355	1.3	5.0		0.5				NF	NF	2 wk
356		7.0		0.3				NF	NF	3 hr
360		9.5		0.5				NF	2 wk	3 hr
380	3.5	9.0						NF	2 wk	2 wk
A612	0.5			0.7	6.5			NF	1 wk	3 hr
C612	0.5			0.35	6.5			NF	NF	3 hr
750	1.0					1.0		1 wk	2 wk	6 hr
APMP**								1 wk	1 wk	3 hr

(1) plus 0.5% Fe

(2) plus 0.5% Pb, 0.5% Bi

* No Failure

** Aluminum powder metallurgy product

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The alloys 18S and 32S showed reasonably low corrosion rates up to 660° F. as shown in Table VIII. Other alloys were satisfactory up to 600° F. The more resistant alloys contained significant amounts of copper, nickel and silicon.

TABLE VIII

AVERAGE ALUMINUM PENETRATION DURING
SIX WEEKS STATIC AUTOCLAVE TESTS

Alloy	480° F.	580° F.	660° F.
18S	2.4 mils/yr.	-----	3.6 mils/yr
32S	3.6 mils/yr	7.2 mils/yr	2.4 mils/yr
2S	failed		

The rates in this table were determined by isolation of the corrosion product film. A 10% solution of reagent grade iodine in absolute methyl alcohol was used to dissolve away the metal as discussed by Pryor and Keir.⁽¹³⁾ X-ray examination of oxide specimens obtained by this technique have shown no change in the hydration of the oxide during the film removal. An oxide replica of the corroding aluminum surface is produced which is very useful in identifying type of attack.

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Grube and Eastwood (14) in their search for an aluminum alloy possessing high temperature strength and corrosion resistance tested many commercial alloys. The compositions of these alloys are listed in Table IX.

These alloys, along with several experimental alloys containing various concentrations of magnesium, were tested in 600° F. static, double-distilled water. None of the alloys had adequate corrosion resistance under these conditions although the copper-containing alloys, 24S and 17S, and the manganese-containing alloy, 3S were markedly superior. High-purity aluminum, 2S, 52S, 61S, 72S, 75S-T Alclad and R317 all had very poor resistance to corrosion at 600° F.

Static tests on 75S aluminum (5.5% Sn, 2-5% Mg, 1-5% Cu, 0.3% Cr and 0.2% Mn), were conducted for about 500 hours in degassed, de-ionized water at 400° F. and 500° F. (10) The samples remained intact with weight change rates of about 0.46 and 1.7 mg/cm²/mo at 400° F. and 500° F., respectively.

Strom and Boyer (15) tested the alloys listed in Table X at 350° F. and 480° F. in static distilled water. The designation after the hyphen, such as T6, indicates the manufacturer's heat treatment. High initial rates were observed which dropped off rapidly to nearly constant penetration rates of less than 0.3 mils/yr at 350° F. and about 1 to 3 mils/yr at 480° F. Alclad 24S, containing 4.5% copper, clad with pure aluminum, was the most resistant of the alloys tested.

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TABLE IX
CHEMICAL-COMPOSITION LIMITS FOR COMMERCIAL
WROUGHT ALUMINUM ALLOYS USED IN CORROSION TESTS*

Alloy	Cu	Si	Fe	Mn	Mg	Zn	Cr	Others
2S(1)	0.20	(2)	(2)	0.05	-	0.10	-	0.15
3S	0.20	0.60	0.70	1.0-1.5	-	0.10	-	0.15
17S	3.5-4.5	0.80	1.00	0.4-1.0	0.2-0.8	0.10	0.10	0.15
24S	3.8-4.9	0.50	0.50	0.3-0.9	1.2-1.8	0.10	0.10	0.15
52S	0.10	(3)	(3)	0.10	2.2-2.8	0.10	0.15-0.35	0.15
61S	0.15-0.40	0.4-0.8	0.70	0.15	0.8-1.2	0.20	0.15-0.35	0.15(7)
72S	0.10	(4)	(4)	0.10	-	0.75-1.25	-	0.15
75S	1.2-2.0	0.5	0.70	0.30	2.1-2.9	5.1-6.1	0.15-0.40	0.15(8)
R303(5)	1.3	-	-	-	2.5	6.5	0.25	- (9)
R317(6)	3.5-4.5	1.0	1.0	0.40-1.0	0.20-0.80	0.10	0.25	0.15(6)

* Composition in per cent; maximum, unless shown as a range,
balance aluminum

- (1) Minimum aluminum content - 99%.
- (2) Iron plus silicon - 1% maximum.
- (3) Iron plus silicon - 0.45% maximum.
- (4) Iron plus silicon - 0.60% maximum.
- (5) Nominal composition - limits not given.
- (6) Contains 0.3-0.7% each lead and bismuth.
- (7) plus 0.15 Ti
- (8) plus 0.20 Ti
- (9) plus 0.10 Ni

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TABLE X
NOMINAL COMPOSITION OF WROUGHT ALUMINUM ALLOYS

Alloy	Cu	Si	Mn	Mg	Zn	Cr
2S	99.0% Al	(Min.)				
24S	4.5		0.6	1.5		
61S	.25	0.6		1.0		0.25
52S				2.5		0.25
72S	1.6				1.0	
75S			0.2	2.5	5.6	0.3

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IV - ANODIC PROTECTION OF 2S ALUMINUM

Draley and Ruther (16) noticed that although 2S aluminum samples exposed to distilled water at 600° F. disintegrated after just a few hours, resulting in a heap of aluminum oxide on the bottom of the test autoclave, aluminum gaskets used on the stainless steel autoclaves showed only relatively low corrosion. Since the gaskets were exposed to steam while the samples were under the surface of the liquid, the results were even more surprising. To determine reasons for this phenomenon, 2S aluminum was electrically coupled to stainless steel. The onset of "blister" corrosion was reduced greatly, extending the lifetime of the aluminum in 600° F. water. The same protective action was observed when zirconium was used as the cathodic metal in the couple. Current measurements between samples of 2S aluminum and the stainless steel or zirconium protecting it from rapid corrosion showed that the latter metals were cathodic to the aluminum, so that this could be termed "anodic protection".

The mechanism of anodic protection, whether by inhibitor, electrical, or alloying, is to promote a generalized attack which is preferable to localized attack that might result in blistering or pitting.

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No suppressing of blister attack was noted for any combination of pH and oxidizing agent, such as dichromate or other successful low temperature inhibitors. Therefore, the important effect in anodic protection was assumed to be the movement of the cathodic corrosion reaction (liberation of hydrogen) away from the aluminum. Since this greatly slowed the blistering, the cathodic reaction was considered responsible for the most damaging type of attack on aluminum. This beneficial effect might in part be counterbalanced by metal loss depending on the geometry.

Hydrogen ions from the solution are postulated to diffuse through the aluminum oxide barrier layer and are reduced to atomic hydrogen at the metal-oxide interface. (16) The hydrogen atoms may combine to form molecules or diffuse into the metal and probably neither the atoms nor molecules can readily diffuse back out through the oxide film. At elevated temperatures a significant fraction is assumed to diffuse into the metal and collect at rifts or cavities to form non-diffusing molecular hydrogen. Pressure builds up within these rifts, cracking or bulging the soft metal into blisters. When these blisters rupture, water is admitted to the fresh metal, producing more hydrogen at a point considerably below the normal metal surface. This process thus may become self-accelerating as is noted experimentally.

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V - SOLUTION PROTECTION

One of several means used to provide cathodes was the addition of reducible metal ions to the test solution. (16,17) Depending on the pH of the solution, a range of 5 to 50 ppm of Co^{++} , Cd^{++} , or Ni^{++} will serve as "remote cathodes" to seemingly prevent "blistering". However, for reactor applications, cobalt and cadmium have undesirable nuclear properties. The applicability of nickel is limited by the low solubility of the basic nickel salts. Unless the pH of the solution is reduced to a point where the solubility product of the basic salt is not exceeded, deposition of the nickel will occur throughout the system and must be continuously replenished. Short-time tests indicate that 5 ppm of Ni (as NiSO_4) at a pH of 3.5 is adequate to prevent any blistering, and that this solution is not depleted by its passage through an autoclave nor will deposition occur. The corrosion rate of 2S aluminum in 525° F. water containing 5 ppm nickel as NiSO_4 additive (pH 3.5) was only 0.41 mils/yr (.25 mg/cm²/mo). After a 70-day test the samples were in excellent condition, with no discernable deposits on either the samples or autoclaves.

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VI - PLATING PROTECTION

Another method of anodic corrosion protection tried for 2S aluminum was plating with films of nickel using the "Kanigen" dip process.^(10.16) A piece of plated 2S tubing was deliberately bent to crack the nickel plate following which the metal was ground free of the plating on a 1/32 inch cross section to determine if a complete or an impervious plate was required to prevent blistering. A 25-day static corrosion test at 600F produced no blisters in the exposed 2S aluminum and indicated that protection could be achieved without complete coverage, which correlates well with solution protection experiments.

Tests were run in high temperature dynamic loops using 2S aluminum samples plated by the same process with two thicknesses of nickel; namely, 0.0003-0.0004 inch and a thinner flash coat of about 0.0001 inch. The adhesion on the flash samples was so poor, some plate was inadvertently removed with a piece of Scotch tape. One set of samples (5 of the 0.0003 inch and 5 of the flash coat) were run for 18 days in distilled water at 525F. Flow rate was 15-20 ft/sec. All the samples were covered with a thin, dark, uniform coat. No pits or other signs of unusual attack were noted on the heavier plates. The flash-coated samples had small shallow pits on one end. No corrosion rates could be deduced from the weight changes, which were small and erratic. In general, both plates changed by less than 1 mg/cm².

Additional samples of nickel plated 2S aluminum (the same plating thicknesses as above) were tested in 600 F degassed, deionized water at 18 fps. Samples with a 0.0003 inch Ni plate accumulated a total of 2625 hours of

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exposure; those with electroplated Ni. 0.001 inch in thickness received a total exposure of 1650 hours. Results are given in Table XI⁽¹⁰⁾. It will be noted that one of the heavier Kanigen-plated (.0003 inch) samples failed between 985 hours (41 days) and 1250 hours (52 days) and one of the still more heavily electroplated (.001 inch) samples failed after 1298 hours (54 days) testing. For the four Kanigen plated (.0003 inch) surviving 2625 hours, the average corrosion rate was $0.19 \text{ mg/cm}^2/\text{mo}$. For the electroplated samples (0.001 inch) surviving 1640 hours, the average corrosion rate was $0.06 \text{ mg/cm}^2/\text{mo}$. These rates closely approach those of zirconium.

Flash-coated specimens (.0001 inch) were also tested, although rate change rates for these are not given in Table XI. One failed by disintegration within 5.7 days and at 41 days the rest were removed, since one other had failed and all showed signs of impending failure. As the flash samples were removed, they were replaced with 0.0003 inch nickel samples previously tested at 525 F; results for one specimen are included in the table (sample No. K6). One of these replacements developed a large blister after 12 days and was removed.

Two samples of 2S aluminum plated with nickel by the Kanigen process (0.0003 inch) and two samples nickel electroplated (.001 inch) were irradiated in a loop in the MTR for 530 hours in 500 F water. The samples had additional periods of 50 hours at 450 F and 150 hours at 350 F. Total integrated flux was 5×10^{20} nvt. The examination showed that much of the Kanigen and electroplated nickel had been corroded and flaked away, exposing the

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TABLE XI

CORROSION OF NICKEL-PLATED 2S ALUMINUM IN 600 F WATER AT ABOUT 18 FPS

<u>No.</u>	<u>306 hrs.</u>	<u>1250 hrs.</u>	<u>1924 hrs.</u>	<u>2625 hrs.</u>
1	-0.776	-0.645	-0.019	0.05
2	-0.653	-0.388	0.000	0.06
3	-0.224	0.077	-0.152	0.30
4	-1.16	Ruptured (1)		
5	-1.33	0.00	0.295	0.351
6			<u>674 hrs.</u> 0.152	<u>1375 hrs.</u> 0.381
7		<u>265 hrs</u> 0.129	<u>939 hrs.</u> 0.809	<u>1640 hrs</u> Blistered
8		-0.323	-0.019	0.12
9		-0.31	0.00	0.05
10		-0.323	-0.219	0.05
11		-0.233	-0.286	0.07
12		-0.452	-0.133	0.03
13		-0.323		
14		-0.336		
15		-0.401		
16		-0.478		

Samples 1-6 Nickel-plated by Kanigen process, about 0.3 mil. thick
Samples 7-16 " " " electroplating process, Film 1 mil thick
(1) Replaced by Sample 6 which was previously tested at 525 F for 95
and 336 hr with weight change rates of -1.01 and -0.184
mg/(cm²)(mo), respectively

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underlying aluminum to corrosive attack. When the samples were removed they were heavily coated with black magnetic iron oxide which was very difficult to remove, leaving some question as to the actual corrosion rates.⁽¹⁹⁾

Tests at Hanford in which Kanigen nickel plated 2S aluminum was irradiated in pile for 40 to 50 days gave no indication of the nickel peeling off.⁽²⁰⁾ The nickel had been deposited by means of a zinc displacement layer; the plates were not covered with magnetic iron oxide at the end of the test. The plating method probably explains the difference in results obtained at Hanford and the MTR. Corrosion rates were very low in the Hanford tests.

Since the Hanford tests were based on a larger number of samples, it would seem as though electroless nickel plating (Kanigen) can be made to adhere to aluminum firmly even when irradiated in pile. Personnel⁽²¹⁾ experienced in Alcoplating (electroless nickel plating) have stated that the nickel coat should be at least 0.5 mils thick for good adhesion and zero porosity.

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VII - ALUMINUM-NICKEL ALLOYS

One of the most promising means of providing protection against blistering developed by Draley and Ruther^(16,22) was the selection of nickel as an alloying agent. Based on their theory, the nickel provides a second phase, of low hydrogen overvoltage, to act as local corrosion cathodes for the rest of the aluminum grain. In a preliminary experiment, specimens of 2S containing 0.01, 0.1, and 0.3 w/o Ni were cast, cold worked, and exposed to distilled water at 550 F. Even the 0.01% sample showed some corrosion improvement over typical 2S performance while the 0.3% Ni sample developed only two clusters of blisters at the corner after 17 days; the rest of the surface was in good condition. Ordinary 2S would be largely converted to oxide by this exposure.

Two commercial aluminum-nickel alloys, both produced by Alcoa, have been chiefly evaluated in dynamic corrosion loops--M-388 and M-400. M-388 is nominally 1% Ni in a 2S base; M-400 is 1% Ni, 1% Fe in a 2S base. The nominal compositions are given in Table XII; 2S is included for reference.

TABLE XII

CONSTITUENTS

<u>Material</u>	<u>Cu</u>	<u>Fe</u>	<u>Si</u>	<u>Mn</u>	<u>Mg</u>	<u>Zn</u>	<u>Ni</u>	<u>Ti</u>
1100	0.005	0.004	0.004	-	-	-		
M-388	0	0	0	0	0	0.01	1.01	0
M-400	0.10	0.41	0.17	0	0	-	1.07	0.01

(Zero indicates concentration is below detectable limits)

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A. EFFECT OF NICKEL CONTENT

Figure 6 illustrates the effect of varying the nickel content on a series of alloys, while the other variables are held constant. The tests were run in static autoclaves using 600 F distilled water. Since the samples were not stripped of corrosion product, only the weight gain could be measured. Although weight gain curves are not reliable measurements of the actual corrosion rate due to uncertainties as to the composition of the oxide and the amount of oxide lost to the water, they serve well as a preliminary measurement.

Appearance of the samples was uniformly good with smooth, dark corrosion product coats typically formed, which sometimes flaked off during test (see curve for 0.05% Ni). It is possible that prolonged or lifetime testing might point up some difference not noticed in the shorter test. From Figure 5 it was concluded that there was very little effect on the corrosion rate by varying the nickel content from 0.5% to 2.0% if the other variables were held constant.

B. EFFECT OF pH ON Al-Ni ALLOYS

The results of one test at ANL⁽¹⁷⁾ on Al-Ni alloys at 550 F in a replenished autoclave indicated that lowering the pH from 6.7 to 4.6 had a slight adverse effect, changing the corrosion rate from 0.90 mg/cm²/mo to 1.20 mg/cm²/mo. Judging by analogy with unalloyed 2S aluminum the result was unexpected, since reducing the pH at 400 F from 7 to 5 reduced the corrosion rate for the latter from 0.75 mg/cm²/mo to 0.24 mg/cm²/mo. Other tests on Al-Ni

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Figure 6
EFFECT OF NICKEL CONCENTRATION ON THE CORROSION OF NICKEL-
ALUMINUM ALLOYS IN DISTILLED WATER AT 600° F

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alloys in static distilled water at 600 F showed a reduction in corrosion rates from 3.0 mg/cm²/mo (5.3 mils/yr) at a pH of 7 to 1.7 mg/cm²/mo (3 mils/yr) at a pH of 5.⁽²²⁾

C. EFFECT OF TEMPERATURE ON AL-Ni ALLOYS

As expected, the corrosion rate of 0.5%-2% Nickel alloyed in a 2S base increases with the temperature (pH constant). As shown in Figure 6, as the testing temperature is raised, so is the corrosion rate of aluminum-nickel alloys. The data are the results of static and semi-static tests at Argonne^(16,23,24,25), Alcoa Research Laboratory⁽²⁶⁾ and Hanford⁽¹²⁾.

The approximate nature of the tests should be kept in mind when considering the reliability of the corrosion rates in Figure 7. Rates obtained in refreshed systems are probably more accurate than those obtained in static autoclaves since other variables can be kept more constant. The water quality in unrefreshed systems changes considerably from day to day, particularly when less resistant alloys are included in the test, variations of pH from 7.3 to 8.4 having been observed depending on the alloys present. The corrosion of less resistant alloys also gives rise to substantial hydrogen pressures in the autoclave and, as will be discussed later, corrosion rates may possibly be reduced measurably in hydrogenated systems. The testing temperature may also affect the accuracy of measured corrosion rates since the corrosion product becomes increasingly harder to remove as the temperature increases.

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Figure 7

EFFECT OF TEMPERATURE ON STATIC CORROSION
OF ALUMINUM-NICKEL ALLOYS

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D. EFFECT OF FLOW RATE ON Al-Ni ALLOYS

In distilled or deionized water the effect of flow rate (of water past samples) is to increase the corrosion rate of the alloy. When considering rates obtained in a dynamic system, one has to take into account the possibility of erosive effects on samples--particularly on leading edges--due to impurities in the water, even when the total solids content of the water is low. Another effect sometimes noticed ⁽²⁷⁾ is a "wear effect," possibly attributable to vibration, at points where the samples are held in the specimen holder. These erosion-wear effects can usually be noticed by visual examination of the specimens. If not noticed visually, they are usually suspected when the curve of corrosion versus time does not form a straight line.

For aluminum-nickel alloys no appreciable increase in the corrosion rate at 500 F over that of the semi-static condition resulted when the flow rate was increased up to 15 fps. Above flow rates of 15 fps and 500 F, the corrosion rate increases considerably with increases in water velocity so that at 600 F, the rate of 25 fps is over twice the semi-static rate. Above 500 F the pH of the solution also exerts a pronounced effect on the dynamic corrosion rate of aluminum-nickel alloys with increasing temperatures.

This combined pH-temperature effect on the corrosion rate of over 250 specimens of aluminum-nickel alloy M-388 (a nominal 1% Ni in a 2S base) is plotted in Figure 8 for water velocities up to 25 fps--the range most probable in a water-cooled and moderated reactor. Individual points in this figure

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Figure 8
EFFECT OF WATER VELOCITY ON CORROSION OF M-388

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represent the average of many stripped samples, with variations from this average not exceeding 5% and most being less than 3%. The water was initially distilled and deionized. Part of the main water flow was bypassed through a mixed bed demineralizer so as to maintain high water quality in the dynamic loop.

One test conducted at 20 fps and 600 F using only distilled water without the removal of transport corrosion products gave rates over threefold that of the static rate at the same temperature. Part of this increase may be attributed to the possibility that the pH rose into the alkaline range and/or to erosion effects.

E. EFFECT OF HYDROGEN ON Al-Ni ALLOYS

Samples used in dynamic loops at ANL as replacement to hold the same overall test area configuration showed higher corrosion rates by a factor as much as four over originally loaded samples. The higher the velocity the more pronounced was the acceleration of replacement sample corrosion. Whereas the original samples would have a smooth adherent protective scale, the replacement samples had a rougher, ruptured scale^(24,25).

A correlation appeared to exist between increased replacement sample corrosion and the hydrogen gas content of the flowing loop. Aluminum-nickel corrosion was less in the presence of higher hydrogen content, which could account for the replacement sample corrosion problem, since the hydrogen content of the loops is highest in the first two weeks due to the higher initial corrosion rate.

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The effect of hydrogen gas in contact with originally loaded and replacement samples of M-388 was investigated at 600 F and a pH of 5.5 in a loop in which the corrosion product hydrogen was allowed to build up. Little or no difference existed between the stripped corrosion weight losses of originally loaded and replacement samples. Identical results were obtained in a loop operated at the same temperature and at a pH of 7.0, using added hydrogen gas at approximately 200 cc/liter.

In a loop operated with a flow rate of 16 fps at 600 F and at a pH of 7.0, the corrosion rate of 0.5% Ni-2S aluminum was about 13 mils/yr. Under the same conditions but where hydrogen was added, the rate of M-388 was only 8.5 mils/yr. As will be discussed later, the difference in nickel content may partly explain the wide variation, if the alloy contained impurities.

In test loops containing 500 F water (pH = 7.0) at 18 fps, and where evolved hydrogen gas had been allowed to build up, the nominal corrosion rate was about 2. mils/yr (curve (b) Figure 8). In a degassed loop, the corrosion rate was about 11 mils/yr (curve (2), Figure 9). The surfaces of the samples had scaled, ruptured and sloughed off considerably in the latter.

Although it would seem wise to add hydrogen to the primary system of a water cooled and moderated reactor, it is felt that further tests are needed to resolve the effect hydrogen has on the corrosion of aluminum alloys.

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Figure 9 EFFECT OF HYDROGEN ON CORROSION OF M-388

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F. EFFECT OF ADDITIONS TO Al-Ni ALLOYS

The oxidation rate of many metals is sensitive to relatively small additions of certain other alloying metals. The alloying metals are usually of different ionic charge but of equivalent ionic size to the base metal. These alloy metal and base metal ions are considered to substitute for each other in the ionic structure of the oxide, modifying its diffusion characteristics.

Presumably, most alloying constituents are present in an alloy as components in some intermetallic compound. Addition of a third component to a binary system may radically alter the nature of any existing second phase resulting in the formation of an insoluble ternary compound. If this results in passivity of the resulting alloy, an improvement in high temperature corrosion resistance may be expected.

Tests at both Argonne and Alcoa showed that the corrosion resistance of Al-Ni alloys was markedly improved if a 2S base was used instead of high purity metal. This was illustrated in a series of alloys made at ANL using a 0.66% nickel high purity aluminum master alloy to which various additions of iron (0.2-1%) or silicon (0.3-1%) were made⁽²⁸⁾. No deliberate addition of silicon was made to the alloy samples containing iron, and the small amount present was presumed to have come from the ceramic crucible. The ternary alloys of Al-Ni-Si failed in one-day corrosion tests at 660 F in distilled water. The Al-Ni-Fe samples that survived the one-day test were further tested for a total of 6.3 days at 660 F. The metal loss (determined after

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corrosion product removal) is shown in Table XIII. For a nickel alloy of this concentration to have acceptable corrosion resistance, the presence of a small amount of iron appears to be necessary.

TABLE XIII
EFFECT OF IRON ADDITIONS ON THE CORROSION RESISTANCE
OF 0.66% NICKEL-ALUMINUM ALLOY

Corroded 6.3 days in distilled water at 660 F

<u>Alloy No.</u>	<u>Iron</u>	<u>Silicon</u>	<u>Metal Corroded,</u> <u>mg/cm²</u>
126	0.02	0.05	Disintegrated
127	0.21	0.06	3.1*
128	0.58	0.06	3.1*
131	0.95	0.07	2.2*

*Corrected for an estimated 0.2 mg/cm² of film remaining after stripping.

Table XIV shows another study in which a series of alloys were made to determine the minimum iron content necessary to prevent the disintegration at 660 F of a 1/2% nickel alloy. Approximately 0.3% iron was required. Mixed iron and silicon additions were also made to a 1/2% nickel alloy as shown in the last two rows of Table XIV. Iron apparently neutralized the deleterious effects of silicon on the corrosion rate.

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TABLE XIV

EFFECT OF IRON AND SILICON ADDITIONS ON THE CORROSION
RESISTANCE OF A 0.5% NICKEL-ALUMINUM ALLOY IN WATER AT 660 F

<u>Alloy No.</u>	<u>Composition, %</u>		<u>Comments</u>
	<u>Iron</u>	<u>Silicon</u>	
165	0	0.04	Disintegrated (1 day)
164	0.10	0.01	Disintegrated (1 day)
167	0.22	0.01	Areas of surface blistering (1 day)
168	0.31	0.02	No blisters--good condition (1 day)
143	0.3*	0.3*	Some blistering after 6.3 days, metal loss--5.1 mg/cm ² .
150	1.11	0.33	Good condition after 7.7 days, metal loss--2.9 mg/cm ² .

*Nominal - no analysis

To determine whether larger amounts of nickel alone could accommodate the presence of silicon, an Al-4% Ni-1% Si alloy was tested. This alloy was corrosion resistant at 660 F when tested for one day, indicating that increasing the Ni would overcome high silicon contents.

Dillon, Wilson and Troutner⁽¹²⁾ experimented with additions to a binary aluminum alloy to determine if the corrosion resistance could be improved by the presence of other alloying constituents. Tests were run in static distilled water at 660 F and are shown in Table XV.

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TABLE XV
CORROSION OF ALUMINUM-NICKEL ALLOYS

<u>Alloy</u>	<u>% Ni</u>	<u>% Fe</u>	<u>% Si</u>	<u>Time to Failure in 660 F Water</u>
1	0.95	0.01	0.007	24 hours
2	0.66	0.21	0.06	No failure
3	0.47	0.29	0.10	24 hours
4	0.96	0.30	0.11	24 hours
5	1.44	0.30	0.11	No failure
6	1.80	0.28	0.09	No failure

Alloy 1, a binary of high purity aluminum and 1% nickel is not very corrosion resistant. The presence of 0.2% iron in Alloy 2 produces a resistant alloy even though the concentration of nickel is reduced. Small additions of silicon as in Alloys 3 and 4, however, produce a diminution of corrosion resistance which can be compensated for by increased concentration of nickel as in Alloys 5 and 6 or by iron as in Alloy 2. Similar tests at Alcoa indicated the desirability of using 1% Ni in their two aluminum-nickel alloys (M-388 and M-400) produced commercially even though experiments showed that 0.5% might be adequate⁽²⁹⁾.

Aluminum binary alloys containing 2 w/o of lead, tin, bismuth, cadmium, cobalt, iron, copper, or platinum were air-cast and corrosion tested at 600 F. Only the last four elements gave fair results; the other disintegrated. Cobalt and copper alloys were superior to platinum or iron alloys

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but all were inferior to a vacuum-cast 1 w/o nickel alloy⁽¹⁷⁾. The tentative conclusions drawn from this preliminary investigation were:

1. For good corrosion resistance at 660 F, the aluminum-nickel-iron alloy appears to require at least 0.8 w/o total nickel and iron, with a probable minimum nickel content of about 0.4-0.5 w/o.
2. In the presence of silicon, the amount of total nickel and/or iron required to prevent disintegration is greater. Alloys containing silicon appear to have slightly improved adherence between the corrosion coating and the metal. Whether this aids in resistance to flowing water is not known at this time since the effect of silicon in dynamic tests has not been evaluated.
3. A smooth adherent corrosion coating is produced by a fine and uniform dispersion of the second phase in the alloy. Surface roughness upon corrosion occurs when the second phase has agglomerated into larger particles.
4. Using the same melting techniques, Al-Ni-Fe alloys made from a 2S base were superior to those made from a high purity aluminum base. The most promising aluminum-nickel-iron alloy today is M-400, a 1% Ni, 1% Fe in a 2S aluminum base.

As noted in item 2 above, the role played by silicon in the corrosion of aluminum alloys has not been resolved. In their work on binary alloys, Alcoa found (1) no detrimental effect from silicon, and (2) iron was superior to nickel in improving corrosion resistance⁽²⁶⁾. AECL found that the addition

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of 0.1 w/o silicon to high purity aluminum decreased susceptibility to intergranular attack⁽³⁰⁾. Their alloy 6057, which has good mechanical properties at elevated temperatures, is made from a 1S aluminum base (instead of high purity) nominally containing 0.1% Si, 3.5% Mg, 0.002 % Cu, 0.003% Fe, 0.1% Ti and 0.25% Cr. The corrosion rate of this alloy, however, was increased by the further addition of silicon, particularly above 0.43%.

As mentioned previously, Hanford's evaluation of commercial aluminum alloys in high temperature distilled water disclosed that the more resistant alloys contain significant amounts of copper, nickel, or silicon⁽¹²⁾.

The role of silicon definitely needs further evaluation. When present in higher amounts, it possibly reduces the concentration of the protective second phase in the aluminum matrix below a required level by combining with some of the iron or nickel when all are present in the same alloy.

G. EFFECT OF MELTING AND CASTING TECHNIQUE ON Al-Ni ALLOYS

Good melting and casting techniques markedly improve the corrosion resistance of aluminum-nickel alloys. ANL found that alloys made from larger melts such as those produced by Alcoa, showed lower porosity and were more homogenous. Chlorine sparging and chill casting or vacuum melting also decreased the porosity. Grain size studies noted improvement in corrosion resistance for the finer dispersions of the second phase in a given composition alloy and for an increase in the total amount of second phase at a given dispersion.

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H. EFFECT OF WELDING Al-Ni ALLOYS

To determine the weldability of these alloys and the effects of corrosion of the welds, specimens of M-388 were heliarc butt welded using filler rods of the same composition⁽¹⁷⁾. The results of tensile tests on standard tensile specimens are shown in Table XVI.

TABLE XVI

TENSILE TESTS* OF WELDED M-388

<u>Before Corrosion</u> (psi)	<u>After 11.7 Days in Water at 680 F</u> (psi)
17,000	16,600
18,200	17,000

*In each case, break occurred at least 1/2" from weld line.

X-ray and metallographic examination of the welds showed them to be sound, with a smooth transition in microstructure through the welded area. The ease of welding compares favorably with 2S aluminum.

Some of the same material was rolled and spot welded. Two spot welded samples were tensile tested in the annealed condition while two were tested after having been corrosion tested for six days at 660 F. No difference in strength and no unusual corrosion effects were noted.

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I. EFFECT OF HEAT TREATMENT ON Al-Ni ALLOYS

The results of tests to determine the sensitivity of M-388 to heat treatment are given in Table XVII⁽¹⁷⁾.

TABLE XVII

EFFECT OF HEAT TREATMENT OF M-388 ON CORROSION

<u>Heat Treatment</u>	<u>Metal Lost After 13 Days at 600 F in Distilled Water mg/cm²</u>
Annealed 2 hours at 650 F	3.1 3.3
Held 30 minutes at 950 F and water quenched	2.9 2.9
Held 30 minutes at 950 F water quenched and aged 10 hours at 345 F	2.9 2.8

The annealed condition is only slightly less corrosion resistant than the quenched; this finding is concordant with results previously obtained with worked vacuum cast 2S aluminum. Annealed high purity aluminum was invariably subject to attack at temperatures where the annealed metal was somewhat resistant.

J. COUPLING AND CREVICE EFFECTS ON Al-Ni ALLOYS

Tests were performed to evaluate the effect of galvanically coupling Type 347 stainless steel to M-388. Stainless steel bolts and washers were tightened in 1/8" sheets of M-388. After various corrosion periods up to 25 days in distilled water at 600 F, the bolts were removed. No large effects were noted, and no pitting was observed under the washer or in the bolt hole.

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Autoclave work had indicated that aluminum-nickel when coupled to stainless steel Type 304 washers tended to seize together and required hammering to separate. An autoclave experiment was run to evaluate the problem of sticking of fuel element end-box cones into a bottom support plate of stainless steel type 304. Three miniature Al-Ni cones were tested under a unit loading of 3 psi in an autoclave at 414 F and withdrawn at the end of 7, 33, and 44 days, respectively. In no case was any force required for withdrawal. The cones showed evidence of crevice-corrosion pitting which consistently occurred when aluminum-nickel was coupled to stainless steel in a static system. This crevice-corrosion pitting has never been observed in dynamic systems, implicating either differential aeration cells or metal ion cells⁽²⁴⁾.

Two plates of M-388 more or less resembling a tongue and groove, were bound together with aluminum nickel alloy wire or with stainless steel bolts. After testing for a total of 26.7 days in distilled water at 600 F, oxide formation caused sticking, but no serious trouble was encountered separating the units. No pitting was attributed to galvanic corrosion.

K. CORROSION PRODUCTS

Cross section micrographs of M-388 that was exposed for 10 days at 550 F revealed the existence of two distinct corrosion layers⁽³¹⁾. The thickness of the layer adjacent to the metal varied between 10^{-3} and 10^{-5} cm and was translucent, showing imbedded metallic specks. Using modified Kellers etch, these specks were shown to be the second phase constituent of the alloy. Over this compact layer a thicker outer coating of rough texture was noted. While

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the thickness of the compact inner layer varied by a factor of 100 from place to place, the boundary between this layer and the coarse outer coating was a straight line with essentially no dips or rises.

With similar samples exposed 7 days and 30 days at 550 F, the main difference noted was that the compact layer became more uniform in thickness and the metal surface became smoother as time progressed. The thickness of the rather uniform 30 day compact layer was approximately the same as the thicker portions of the 7 day compact layer. Again the boundary line between layers was reasonably straight.

From these observations, in the absence of "blister" attack, two processes appear to be occurring. One is the formation of a fresh compact layer material by oxidation of the aluminum; the other is the transformation of the outer surface of the compact layer into a porous coat. Eventually an equilibrium rate is reached where the rate of growth just equals the rate of degradation. Since the rate of transformation did not seem to be dependent on compact layer thickness, it was probably dependent only on the temperature and the ions in the pores of the coating next to the compact layer.

The thick outer coating breaks away periodically from the surface even in static tests. In dynamic loops, the oxide is also washed off-particularly at higher water velocities. If not removed from the loop, this could possibly cause transport and erosion problems.

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L. IRRADIATION EFFECTS

Generally, irradiation has decreased the corrosion rate of inpile aluminum-nickel alloys in 500 F water ~~as~~ compared with out of pile samples in the same loop. Out of pile samples had rates that compared with those obtained in degassed loops at 500 F; in pile samples at 500 F had rates comparable to loops in which hydrogen was allowed to build up^(18,25,28).

Corrosion rates for slugs jacketed with M-388 in 400 F water were determined at Hanford⁽²⁰⁾. Rates were about the same as for 2S aluminum before "blistering" set in.

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VIII - ALUMINUM-COPPER ALLOYS

Alcoa found that a variety of second phase materials can effectively protect the aluminum matrix. In tests, binary aluminum alloys having up to 6% copper showed favorable corrosion resistance. In ordinary corrosion applications the addition of copper improves the strength but decreases the corrosion resistance, so that these results do appear quite interesting.

ANL corrosion tested aluminum-copper binaries with varying copper contents in static distilled water at 550 F⁽³¹⁾. A 1% alloy suffered "blister" attack and corroded at the fastest rate (not measured due to stripping difficulties). Alloys with 3, 6 and 10% Cu were all pitted at the end of a two week test. The rates (measured from samples with oxide removed after 9 and 14 days) are listed in Table XVIII. As little as 3% copper is thus shown to have some beneficial effect.

TABLE XVIII

CORROSION OF ALUMINUM-COPPER ALLOYS AT 550 F

<u>Alloy</u>	<u>Corrosion Rate</u>
Al-1% Cu	*
Al-3% Cu	3.6
Al-6% Cu	2.04
Al-10% Cu	1.5

*blistered, not measured due to stripping difficulties

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An aluminum-6% copper alloy (X-2219) had good corrosion resistance plus good mechanical properties at elevated temperatures. Based on a 20 week static test in 680 F water at Alcoa, the corrosion rate for this alloy was 3.5 mils/yr ($2.0 \text{ mg/cm}^2/\text{mo}$) as against 9.1 mils/yr for both M-388 and M-400 calculated from short time tests⁽²⁶⁾. The high results for the latter two alloys are probably due to the short time interval over which the tests were conducted.

The corrosion rates for X-2219 in static 30 day tests at Argonne when exposed to 500 and 550 F distilled water were $0.51 \text{ mg/cm}^2/\text{mo}$ (estimated intercept of 0.50 mg/cm^2) and $1.05 \text{ mg/cm}^2/\text{mo}$ for 500 and 550 F respectively. The samples pitted uniformly over the surface although the pits were very small. For comparison, M-388 corrodes at about $0.60 \text{ mg/cm}^2/\text{mo}$ at 500 F and $1.0 \text{ mg/cm}^2/\text{mo}$ at 550 F⁽³²⁾. Six week tests at Hanford in 660 F static distilled water gave no evidence of failure for X-2219; corrosion rates were reasonably low⁽¹²⁾.

Dynamic tests indicated that X-2219 has approximately the same corrosion rate as aluminum-nickel and aluminum-nickel-iron alloys but develops small surface pits under some water conditions. A greater stripped weight loss over that of aluminum-nickel generally was obtained under the same water conditions. Small surface pits and localized erosion-corrosion attack occurred in 16 fps, pH 6.5 unhydrogenated 500 F water; however, no pitting was observed in hydrogenated 600 F water (pH = 7.0). Similar to aluminum-nickel, no signs of erosion-corrosion attack were evident in high velocity water at pH 5.0⁽²⁴⁾. Earlier reports stated that aluminum-copper alloys were

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more sensitive to water velocities than aluminum-nickel alloys⁽²⁵⁾. Recent tests have not shown any appreciable difference⁽³³⁾.

Preliminary KAPL data indicated that X-2219 as well as M-399 and M-400 satisfactorily withstand dynamic corrosion at 680 F and pH's of 5-7⁽²⁷⁾. Long-time dynamic tests (2100 hours) were performed at WAPD on X-2219 at 600 F and pH's of 8.5 - 9.0. Specimens corroded in this alkaline environment under a water velocity of 20 fps at the rate of 7.65 mils/yr (4.4 mg/cm²/mo). M-388 exposed to the same conditions had a rate of 6.76 mils/yr (3.9 mg/cm²/mo)⁽³⁴⁾.

Dynamic tests of X-2219 at ANL have shown about the same weight losses for the alloy at 500 F and 600 F⁽³³⁾. The corrosion rates were slightly lower at a pH of 5 than at 7, as shown in Table XIX.

TABLE XIX

COMPARISON OF X-2219 and M-388
DYNAMIC CORROSION RATES*

<u>Flow Rate</u>	<u>X-2219</u>	<u>M-388</u>
7 fps	6.0 mils/yr	6.2 mils/yr
18 fps	8.0 mils/yr	8.8 mils/yr
*pH-7, 600 F		

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IX - ALUMINUM-NICKEL-TITANIUM ALLOYS

As alloy with improved resistance to 660 F water, the nickel-titanium-aluminum system appears promising. After film removal by the methanol iodine technique, rates were calculated from samples exposed one and three weeks at 660 F in static distilled water. The lowest rate obtained was 1.85 mg/cm²/mo as compared with 4.8 mg/cm²/mo for M-388 under the same conditions⁽³¹⁾.

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X - ALUMINUM-NICKEL-BORON ALLOYS

Since Argonne used 2S aluminum-1% boron-0.5% nickel plates in Borax III to supplement control rods, the corrosion behavior of this material was evaluated. Samples were exposed to 440 F water in static autoclaves for periods up to 335 hours with the pH varying from 8.5 to 5.4. Some samples were prepared by inserting ball-mill mixed powder of 2S aluminum, 1% boron, and 0.5% nickel in a 61S aluminum can and extruding to a 33:1 area ratio. Others were sheets of the material either alone or tack welded at intervals along the edges to 2S sheet. The corrosion rates for these materials are shown in Table XX.

TABLE XX

CORROSION OF Al-Ni-B ALLOYS IN 440 F WATER

<u>Preparation</u>	<u>Corrosion Rate</u>
Ball mill mixed powder	1.59 mg/cm ² /mo
Sheet	0.84 mg/cm ² /mo
Tack Welded to 2S	1.57 mg/cm ² /mo

Attack seemed uniform but tiny pits and blisters were observed. The amount of boron entering the water was small (max. of 0.39 mg/ml) and decreased with time (less than 0.05 mg/ml at end of tests)⁽¹⁰⁾. From their tests it was concluded that from the corrosion standpoint, the use of Al-Ni-B burnable poisons in the matrix was feasible for a water-cooled and moderated reactor.

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XI - SUMMARY

A review of the literature has shown that there are aluminum alloys today that will withstand high temperature aqueous corrosion. The corrosion behavior is particularly affected by the temperature, pH and velocity of the water; the rate was shown to increase with increases in all of these. Other factors affecting the corrosion rate have also been discussed. The corrosion of 2S aluminum in high temperature water can be markedly reduced by either of the following:

1. Plating with nickel
2. Addition of an acid or reducible metal to the water
3. Alloying with nickel, iron, copper and/or titanium

Of these three possibilities, methods 1 and 3 offer the most promise since in the light of present knowledge 2 would require more compromise on the part of the designer of a water-cooled and moderated reactor.

Electroless nickel plated 2S aluminum has been tested at both Argonne and Hanford. Rates in 500 F and 600 F (pH = 7.0) water were 0.30 and 0.40 mg/cm²/mo respectively in short time tests; longer tests showed essentially no weight gains.

Three aluminum alloys that are produced commercially have been evaluated at WAPD, Alcoa, Argonne and KAPL and have been found to have acceptable corrosion rates. These are:

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1. M-388 - 1% Ni in a 2S aluminum base
2. M-400 - 1% Ni in a 2S aluminum base
3. X-2219 - 6% Cu - aluminum alloy

Corrosion rates for these three alloys at various temperatures, pH's and flow rates are summarized in Table XXI.

TABLE XXI
AVERAGE CORROSION RATES IN MILS/YEAR FOR ALUMINUM ALLOYS

Temperature = 500°F

Flow Rate	M-388		X-2219
	pH = 5	pH = 7	pH = 7
Static	1.2	1.3	0.9
Semi-static	1.3	1.5	
6 fps	-	1.5	
7 fps	1.3	1.7	
16 fps	-	2.0	
18 fps	2.1	2.0	
20 fps	2.8	5.5	

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Temperature = 600°F

Flow Rate	<u>M-388</u>			<u>X-2219</u>		<u>M-400</u>
	pH = 5	pH = 7	pH=9	pH = 7	pH = 9	pH = 9
Static	3.0	3.0	-	-	-	
Semi-Static	-	5.3	-	-	-	
6 fps	-	6.3	-	-	-	
7 fps	5.4	6.5	-	6.0	-	
16 fps	-	8.5	-	-	-	
18 fps	7.3	9.0	-	8.0	-	
20 fps	-	10.5	6.8	-	7.7	11.5*, 15.9**
25 fps	-	12.0	-	-	-	

* Heat Treatment - X-14

** Heat Treatment - O

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SECTION II

ZIRCONIUM AND ALLOYS OF ZIRCONIUM

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1 - ZIRCONIUM

Zirconium is usually produced in two major forms - sponge and crystal bar. The "Sponge" is produced from zirconium chloride by the Kroll process; "crystal bar" zirconium, is obtained by refining sponge by the deBoer iodide process. Generally, crystal bar has a higher purity than sponge but is also more expensive.

Crystal bar, being low in non-metallic impurities, is very ductile and easily worked. All unalloyed zirconium lacks strength and has extremely erratic corrosion characteristics, being very sensitive to small amounts of certain impurities. In particular, nitrogen and carbon appreciably reduce the corrosion resistance. However, zirconium's low neutron - absorption characteristics, as shown in Table III of the Appendix, and its relatively good corrosion resistance, make it attractive for reactor applications.

A. MECHANISM

Numerous investigators in their corrosion testing of crystal bar zirconium, noticed that initially a thin adherent protective film of ZrO_2 formed on the specimens. For pure zirconium, this deposit was a loose white powder which could easily be rubbed off. The thickness of the film gradually increased, then quite suddenly changed in character and apparently was no longer protective. A thick white oxide formed on the specimens, accompanied by a resulting sharp increase in the corrosion rate. The time at which the rate increased was generally referred to as "breakaway" time. For

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example, after a zirconium sample had shown excellent resistance for a period of, say, 1000 hours, it might suddenly "breakdown" and corrode at a high rate. The time at which breakdown will occur is unpredictable. This can be illustrated by Figures 10 and 11 (the data are contained in Tables XXII and XXIII) which shows the corrosion resistance in 600°F water of eleven different as-deposited iodide zirconium bars, and seven arc-melted, forged and rolled iodide-zirconium ingots⁽³⁵⁾.

In Figure 10, one sample (18-D-7) had poor resistance from the start, another failed at 500 hours, three failed at 750 hours, and two failed at 1200 hours, while four retained good resistance for 1600 hours. Similarly in Figure 11, "breakdowns" in resistance are noted for the arc-melted iodide samples at unpredictable exposure times. Some failed after relatively short exposures (Z649, C-23), others after somewhat longer exposures, while Z510 still showed a good corrosion rate and no white oxide after 3574 hours.

Chemical analysis does not furnish any data on which the time of breakdown can be predicted. This is illustrated in Table XXIV which gives chemical and spectrographic data for three of the specimens (J-2, J-7, 18-D-7) shown in Fig. 10. No significant differences are evident in the chemistry of these three that would account for the differences in corrosion behavior.

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Weight Gain, mg / cm²

FIGURE 10. CORROSION BEHAVIOR OF AS-DEPOSITED IODIDE ZIRCONIUM DURING EXPOSURE TO 600°F WATER (1500 ps.i.)

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Figure 11
CORROSION BEHAVIOR OF ARC-MELTED IODIDE ZIRCONIUM DURING EXPOSURE TO 600° F WATER (1500 psi)

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TABLE XXII
CORROSION OF AS-DEPOSITED IODIDE CRYSTAL BAR ZIRCONIUM
IN 600 F WATER, 1500 PSI
WEIGHT GAIN IN MG/CM²

Sample No.	Exposure Time, Hours					
	<u>40</u>	<u>305</u>	<u>500</u>	<u>750</u>	<u>1217</u>	<u>1630</u>
J-1	0.00	0.06	0.06	0.06	1.01	0.97
-2	0.03	0.11	0.09	0.09	0.74	1.50
-4	0.03	0.10	0.08	0.08	0.10	0.20
-5	0.03	0.13	0.13	0.12	0.10	0.23
-6	0.03	0.09	0.09	0.09	0.12	0.94
-7	0.03	0.08	0.07	0.08	0.10	0.63
-8	0.03	0.09	0.09	0.12	1.24	2.16
-10	0.03	0.07	0.07	0.08	0.18	0.23
-11	0.03	0.10	0.08	0.08	0.17	0.22
-12	0.05	0.11	0.11	0.40	0.97	1.61
	<u>74</u>	<u>350</u>	<u>950</u>	<u>1240</u>	<u>1340</u>	
18-D-7	0.17	0.27	0.70	1.12	1.53	

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TABLE XXIII
CORROSION OF ARC-MELTED, ROLLED, AND FORGED ZIRCONIUM
IN 600 F WATER, 1500 PSI
WEIGHT GAIN IN MG/CM²

Ingot No.	<u>Exposure Time in Hours</u>									
	<u>50</u>	<u>150</u>	<u>192</u>	<u>250</u>	<u>400</u>	<u>513</u>	<u>666</u>	<u>1016</u>	<u>1236</u>	<u>3574</u>
Z510	0.12	-	0.16	-	0.16	-	0.16	0.16	0.15	0.45
2518	0.13	0.13	0.13	0.16	0.40	0.58	0.94	1.84	6.78	-
2521	0.13	0.13	0.13	0.13	0.21	0.24	0.51	1.18	1.60	-
2649	0.22	0.42	-	-	0.75	-	-	-	-	-
2627	0.15	0.24	-	-	0.29	-	0.29	1.00	-	-
2572	0.07	-	-	-	0.07	-	0.20	0.90	1.01	-
	<u>45</u>	<u>170</u>	<u>260</u>	<u>345</u>	<u>610</u>	<u>910</u>	<u>1410</u>	<u>1695</u>		
C-23	0.05	0.28	0.34	0.65	1.35	2.25	3.31	4.00		

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TABLE XXIV
ANALYTICAL AND SPECTROGRAPHIC DATA
FOR AS-DEPOSITED IODIDE ZIRCONIUM

Sample No.	<u>C</u>	<u>N</u>	<u>Sn</u>	<u>Al</u>	<u>Fe</u>	<u>Ti</u>	<u>Si</u>	<u>Mn</u>	<u>Cu</u>	<u>Pb</u>	<u>Co</u>		
J-2	300	10	*10	100	100	*10	100	*1	5	5	-		
J-7	200	10	*10	50	70	25	110	*1	7	5	-		
18-D-7	230	5	* 5	40	360	*10	110	*5	10	30	*5		
	<u>Zn</u>	<u>Cr</u>	<u>Cd</u>	<u>B</u>	<u>Mg</u>	<u>Ca</u>	<u>Mo</u>	<u>Ni</u>	<u>V</u>	<u>Be</u>	<u>W</u>	<u>HF</u>	<u>Ta</u>
J-2	-	10	*10	3	20	*10	65	35	*10	*1	*50	24,500	-
J-7	-	10	*10	4	10	*10	75	20	*10	*1	*50	23,000	-
18-D-7	*100	20	*10	2	*10	*10	10	90	*10	*1	*50	21,000	*500
* less than													

The above examples, illustrating the erratic and spotty corrosion behavior of zirconium in 600°F water, are not just a few "unusual" cases observed. Tables XXV and XXVI contain a summary of the corrosion behavior in 600°F water of 83 arc-melted iodide zirconium samples and 323 as-deposited iodide zirconium samples⁽³⁵⁾. Of the 83 arc melted specimens, 40 or 48.1

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TABLE XXV

"BREAKDOWN" OF ARC-MELTED IODIDE ZIRCONIUM

# of Speci- mens in Group	# and % Showing No. White Oxide		% and No. Showing "Breakdowns" During Indicated Exposure Periods											
			0 to 350 Hrs.	351 to 1000 Hrs.	1001 to 2000 Hrs.	2001 to 3000 Hrs.	3001 to 4000 Hrs.	4001 to 5000 Hrs.						
	#	%	#	%	#	%	#	%	#	%	#	%	#	%
83	43	51.9	7	8.4	17	20.5	12	14.4	2	2.4	1	1.2	1	1.2

# of Speci- mens in Group	# and % Showing No. White Oxide		% and No. Showing "Breakdowns" During Indicated Exposure Periods											
			0 to 350 Hrs.	351 to 1000 Hrs.	1001 to 2000 Hrs.	2001 to 3000 Hrs.	3001 to 4000 Hrs.	4001 to 5000 Hrs.						
	#	%	#	%	#	%	#	%	#	%	#	%	#	%
323	253	78.3	15		47		8		0	0.0	0	0.0	0	0.0

TABLE XXVI

"BREAKDOWN" OF AS-DEPOSITED IODIDE ZIRCONIUM

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per cent showed white oxide and breakdown in corrosion resistance at some unpredictable exposure time. In the case of the 323 as-deposited specimens, 70 or 21.7% showed white oxide at some unpredictable time. Considering both arc melted and as-deposited specimens, of a total of 406 samples, 110 (27.1%) showed white oxide or exhibited a "breakdown" in resistance, and, of this number, 21 or 19.0% failed within a 2-week test period.

Obviously the corrosion resistance of zirconium in a short-time test (e.g., 350 hours or less) does not necessarily give an accurate indication of the corrosion behavior for more extended exposure periods. If zirconium were selected for a reactor solely on the absence of visible white film after two weeks in 600°F water, it is possible that a substantial white corrosion product would form on some of this material during the life of the reactor. Tests showed that raising the temperature to 650°F (2200 psi) of either water or wet steam did not result in any marked acceleration of the corrosion of good-quality zirconium⁽³⁵⁾.

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Work at Battelle⁽³⁵⁾ showed that "breakdown" of zirconium was accelerated by exposure to 750°F steam and that this could be used to quickly eliminate samples that would eventually "breakdown" in 600°F water. After verification by other investigators, such as at MIT and ANL, the 750°F steam test was proposed⁽³⁶⁾ as an "acceptance test" for zirconium. Samples surviving two weeks in 750°F steam will probably not show evidence of "breakdown" for extended periods of time in 500-600 F. water. Even "preselection", though, will not insure the absence of breakaway as illustrated in Table XXVII for "pre-selected corrosion resistant zirconium" tested in 600°F. degassed, distilled water⁽³⁷⁾.

TABLE XXVII

STATIC 6-MONTH TEST OF SWAGED PRESELECTED CORROSION
RESISTANT CRYSTAL BAR ZIRCONIUM

<u>Total Test Time (Hrs)</u>	<u>Corrosion Rate (mg/cm²/mo)</u>
355	0.04
1005	0.10
1677	0.02
2429	0.04
3149	0.15
3913	0.04
4799	1.24

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B. EFFECT OF WATER COMPOSITION

Tests on low hafnium crystal bar zirconium exposed for 6 months to static distilled water containing dissolved O_2 , H_2 , H_2O_2 , KOH, and HNO_3 at 600 F gave the results shown in Table XXVIII⁽³⁸⁾.

TABLE XXVIII
CORROSION RATES OF ZIRCONIUM TESTED IN
VARIOUS WATER COMPOSITIONS AT 600 F

<u>Water Composition</u>	<u>Corrosion Rate(mg/cm²/mo)</u>
1. Degassed, Distilled	✓ 0.96
2. Distilled water with O_2 at 120 psi	✓ 0.04
3. Distilled water with H_2 at 60 psi	- 0.45
4. Distilled water with 0.5% by weight H_2O_2	- 0.09
5. Distilled water with 1.0% by weight H_2O_2	✓ 0.19
6. Distilled water with KOH to give pH 10.6	✓ 0.11
7. Distilled water with HNO_3 to give pH 4.0	✓ 0.11

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Degassed, distilled water was the most corrosive ^{along} with water containing dissolved hydrogen. For comparison, the average corrosion rate of a single specimen of crystal bar zirconium exposed for 6 months to static distilled water at 600 F was determined to be $\neq 0.29 \text{ mg/cm}^2/\text{mo}$, as shown in Table XXIX (38). This rate is equivalent to an average dimensional increase of 0.3 mils/yr, assuming the corrosion product is zirconium oxide with a density of 5.71.

TABLE XXIX
CORROSION RATES OF CRYSTAL BAR ZIRCONIUM
IN STATIC, DISTILLED, 600 F WATER

<u>Time</u> <u>(Hrs.)</u>	<u>Cumulative Unit Weight</u> <u>Increase (mg/cm²)</u>	<u>Corrosion Rate for Each</u> <u>Test Period (mg/cm²/mo)</u>
355	$\neq 0.27$	$\neq .54$
686	$\neq 0.61$	$\neq .74$
1041	$\neq 0.38$	- .47
1351	$\neq 0.55$	$\neq .37$
1652	$\neq 0.55$	$\neq .00$
2079	$\neq 0.99$	$\neq .74$
2434	$\neq 0.99$	$\neq .00$
2605	$\neq 1.07$	$\neq .34$
3370	$\neq 1.35$	$\neq .26$
4070	$\neq 1.62$	$\neq .27$

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C. CORROSION PRODUCTS

The residual water remaining after test of the sample in Table XXIX was chemically analyzed for pickup of corrosion products. The change in water composition following the six month test is summarized in Table XXX⁽³⁸⁾. For comparison, spectrographic and chemical analysis of arc-melted crystal bar zirconium is listed in Table XXXI⁽³⁹⁾.

TABLE XXX

TEST WATER ANALYSIS

<u>Composition</u>	<u>Initial</u>	<u>Final</u>
pH	6.5 - 7.0	6.3
Resistivity	250,000 ohms	85,000 ohms
Total Solids	5.0 ppm	10.0 ppm
Organic and Volative	3.5 ppm	6.8 ppm
Fixed Residue	1.5 ppm	3.2 ppm

<u>FIXED RESIDUE ANALYSIS (IN PPM)</u>					
	<u>Initial</u>	<u>Final</u>		<u>Initial</u>	<u>Final</u>
Iron	0.5	1.5	Sn	0.05	0.05
Cr	0.02	0.05	Si	0.50	0.50
Ni	0.02	0.06	Zr		
Ca	0.25	0.50	Pb	trace,	trace
Mg	0.05	0.25	Cu	- ,	0.02

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TABLE XXXI
SPECTROGRAPHIC AND CHEMICAL ANALYSIS OF A REPRESENTATIVE
SPECIMEN OF FOOTE ARC MELTED CRYSTAL ZR

	Major
Zr	
C	.05
N	.005
O	.043
Mg	.001
Fe	.075
Al	.007
Hf	.04
Ni	.006
Ti	.002
Cu	.001
Cr	.003
Mn	.0008
Pb	.003
Sn	*.003
Si	.005
V	*.001
Gd	*.00005
B	.00002

* Less than

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D. EFFECT OF WATER VELOCITY

Dynamic tests in 600 F water on tensile bars machined from welded crystal bar zirconium indicated that water velocities up to 50 fps and stresses to 5000 psi did not appreciably increase the corrosion rate⁽⁴⁰⁾⁽⁴¹⁾. Experiments of over 2500 hours duration in dynamic loops containing 25 cc/l of dissolved hydrogen in the water showed the corrosion rate of crystal bar zirconium to be less than 0.2 mg/cm²/mo at both 500 and 600 F⁽³⁷⁾⁽⁴⁰⁾⁽⁴²⁾. This is less than half the rate obtained in static systems. The rates in hydrogenated loops were greater than in oxygenated and degassed loops.

E. EFFECT OF TEMPERATURE

Tests have shown that increasing temperatures in the range of 500 to 650 F increases the corrosion rate of zirconium. Dynamic tests have shown a slightly greater effect; rates at 600 F were occasionally 1.5 times as severe as at 500 F. Weight gains for zirconium exposed to various water and steam temperatures are shown in Table XXXII and Figure 12⁽⁴³⁾.

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Figure 12
EFFECT OF TEST TEMPERATURE ON CORROSION BEHAVIOR OF ZIRCONIUM

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TABLE XXXII

EFFECT OF TEMPERATURE ON CORROSION OF ZIRCONIUM

540°F		600°F		680°F		750°F (Steam)	
Exposure Time (Hr)	Wt. Gain Mg/cm ²	Exposure Time (Hr)	Wt. Gain Mg/cm ²	Exposure Time (Hr)	Wt. Gain Mg/cm ²	Exposure Time (Hr)	Wt. Gain Mg/cm ²
1395	0.29	666	0.86	50	0.69	-	-
.50	0.73	50	1.64	60	11.5	-	-
1100	0.93	350	1.24	50	1.28	18	3.63
1100	0.28	463	0.78	50	1.29	18	2.63
1100	0.33	1088	0.75	100	0.80	72	2.35
1395	0.15	1340	0.39	-	-	18	0.15
1355	0.34	1270	0.26	-	-	18	0.20
-	-	3603	0.20	1200	0.50	18	0.35

Based on these and other tests ⁽³⁷⁾, the Mark I was designed on the rates shown in Table XXXIII and Figure 13. Average rates of 10 representative specimens in degassed, distilled water are listed for various temperatures ⁽⁴⁴⁾.

TABLE XXXIII

CORROSION OF ZIRCONIUM IN DEGASSED, DISTILLED WATER

Temperature (°F)	Corrosion Rate (mg/cm ² /mo)
500	0.15
550	0.21
600	0.29
650	0.43

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Figure 13

EFFECT OF TEMPERATURE ON CORROSION RATE OF
ZIRCONIUM

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The best zirconium currently being produced will maintain a corrosion rate of less than $0.10 \text{ mg/cm}^2/\text{mo}$ for several thousand hours in 600°F water. The weight gain initially is a little higher and may be as high as $0.20 \text{ mg/cm}^2/\text{mo}$. Tests in 600°F water have shown an average rate for 5000 hours of $0.05 \text{ mg/cm}^2/\text{mo}$ (46).

F. EFFECT OF HEAT TREATMENT

The effect of heat treatment on the corrosion behavior of zirconium has not been well established. However, it has been shown that, although rapidly quenching from, or annealing above the transformation temperature does not retain the beta phase, it does result in poorer corrosion resistance than annealing in the alpha-phase field. Tests in 680°F water indicated maximum corrosion resistance could be obtained by annealing in the range 800° to 875°C (45).

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G. EFFECT OF IMPURITIES

The corrosion resistance of zirconium in water or steam is very sensitive to the amounts of other elements which are present in the zirconium. Certain elements have an adverse effect on the corrosion resistance, many have no effect, and a few are definitely beneficial.

Certain materials are known to be very harmful to the corrosion resistance of zirconium in 600°F water. Zirconium is apparently most sensitive to the effects of nitrogen, even in minute amounts, and since zirconium is avid for nitrogen, it is difficult to maintain very small amounts of this element in the metal. Initial degassing of test water has been found essential, nitrogen in the water being as injurious as nitrogen in the metal. Nitrogen concentrations as low as 30 ppm have been reported⁽⁴⁷⁾ to have detrimental effects, 50 ppm causes a noticeably adverse effect and the material is very poor when the nitrogen is 100-200 ppm⁽⁴⁶⁾. Table XXXIV gives the corrosion rates at 600°F for 1200 hours of good quality, preselected normal hafnium-bearing crystal bar metal with varying nitrogen contents introduced by vacuum diffusion⁽⁴⁷⁾.

TABLE XXXIV

EFFECT OF NITROGEN ON AS-DEPOSITED IODIDE ZIRCONIUM

<u>Nitrogen Range, ppm</u>	<u>Corrosion Rate, mg/cm²/mo</u>
5-20	0.06 - 0.13
30-50	0.15 - 0.45
70-80	0.63 - 1.0
60-170	5.0 - 13.0

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Carbon is also very detrimental to the corrosion resistance of zirconium, although the effect is generally unpredictable since the size and distribution of the carbide inclusions affect its tolerance limit. MIT noticed the adverse effects of carbon in 1947 when graphite crucibles were used to melt zirconium in place of arc-melting. Arc-melting is not particularly suited to producing homogeneous alloys since only part of the melt is molten at any one time and to overcome this it is necessary to arc-melt at least twice using a consumable electrode, which increases the costs.

Microscopic examination revealed that corrosion started as a local attack on the individual carbide particles at water temperatures as low as 250°F⁽⁴⁸⁾. Further tests showed more carbon could be tolerated if distributed throughout the grains than if the particles formed a network at grain boundaries. Even heat treating, except melting, and the addition of alloys, did not seem to prevent the attack on the carbides themselves.

Although graphite-melted zirconium is cheaper and more homogenous than arc melted, the carbon pickup has limited its use. Nitrogen can also be introduced from the atmosphere unless the crucible is outgassed in a vacuum for several hours at about 2130°C. This is illustrated in Table XXXV for pre-tested crystal bars melted in graphite crucibles - one lot in an as-machined crucible, the other in a similar outgassed crucible - and subsequently tested in 600°F water⁽⁴⁷⁾.

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TABLE XXXV
EFFECT OF CRUCIBLE OUTGASSING ON CORROSION
RESISTANCE OF GRAPHITE-MELTED ZIRCONIUM

Crucible	Analysis		Wt. Gain after indicated hrs. (mg/cm ²)			
	C (ppm)	N ₂ (ppm)	413	991	1235	2300
As machined	2700	120	105.0	-	-	
Outgassed	1400	20	0.10	0.15	0.15	Still good

Other impurities which have an adverse effect include aluminum and titanium. The actual limit for aluminum concentration without deterioration of corrosion resistance is not known. Zirconium with 2000-3000 ppm (0.2-0.3%) had definitely poor resistance; aluminum contents of less than 100 ppm generally had no detrimental effect⁽⁴⁷⁾. One week tests at 600°F of zirconium containing various concentrations of aluminum gave the results shown in Table XXXVI⁽⁴⁹⁾. For titanium, a tentative limit of 80 ppm has been set; however, tests indicated that at least 275 ppm of titanium can be tolerated, but that 1500 ppm is harmful⁽⁴⁹⁾.

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TABLE XXXVI

EFFECT OF ALUMINUM ON CORROSION RESISTANCE OF ZIRCONIUM

<u>Al Content (wt.%)</u>	<u>Weight Gain (mg/cm²)</u>
0.00	14.6
0.05	203.5
0.10	394.0
0.20	696.0
0.30	Severely attacked

With proper techniques, chlorine should not be present in any finished zirconium, since it can be readily removed from melted or extrusion stock by a vacuum-annealing treatment; however, if it is present, it is detrimental to corrosion resistance. Iodide zirconium containing less than 100 ppm chlorine corroded very rapidly - 0.37 and 0.78 mg/cm² in 21 and 185 hours respectively⁽⁴⁹⁾.

Oxygen concentrations up to 200 ppm are commonly encountered in zirconium but it does not seem to be detrimental. Some investigators report that zirconium is not impaired by additions of oxygen up to 0.4 wt%; others indicate, as shown in Table XXXVII that the presence of oxygen up to 1% has little effect.

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TABLE XXXVII
EFFECT OF OXYGEN ON THE CORROSION RESISTANCE OF ZIRCONIUM

<u>O₂ Content (wt %)</u>	<u>Weight Gain (mg/cm²)</u>
0.041	1.53
0.044	1.29
0.059	1.50
0.073	1.21
0.105	1.31
0.445	1.43
1.002	1.27
Average	1.36

Zirconium normally contains about 50 ppm of hydrogen although concentrations up to 1000 ppm are encountered. Hydrogen does not seem to be detrimental to the corrosion resistance of zirconium and samples of ZrH₂ are not badly attacked in water⁽⁴⁹⁾. Qualitatively, however, strain induced porosity in zirconium seems to be associated with the hydrogen content. The presence of hydride due to slow cooling or strain aging gives rise to porosity, while hydrogen in solution leads to non-porous fractures⁽⁵⁰⁾.

Many of the materials which might be found as impurities in zirconium appear to have little effect on corrosion resistance. These include cobalt, molybdenum, tungsten, lead, zinc, thorium, vanadium and beryllium⁽⁴⁶⁾.

Small amounts of tantalum, iron, and niobium appear to improve the corrosion resistance of zirconium. Two-week tests in 600°F water of sponge zirconium containing 0-0.3% Ta gave the rates shown in Table XXXVIII; in concentrations over 0.6%, however, tantalum seemed to be detrimental⁽⁴⁹⁾.

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TABLE XXXVIII

EFFECT OF TANTALUM ON CORROSION OF ZIRCONIUM

<u>Tantalum, wt.%</u>	<u>Corrosion Rate, mg/cm²/mo</u>
None	2.6
0.1	0.6
0.2	0.18
0.3	0.15

Based on these and other tests, the zirconium for the Mark I had the impurity specifications shown in Table XXXIX⁽⁴⁶⁾. More recent tests have estimated upper tolerance limits for impurities so shown in Table XL⁽⁴⁷⁾.

TABLE XXXIX

SPECIFICATIONS FOR IMPURITIES IN ZIRCONIUM

<u>Element</u>	<u>Limit, ppm</u>
Carbon	500
Nitrogen	100
Oxygen	1700
Magnesium	20
Aluminum	200
Silicon	820
Chlorine	15
Calcium	25
Titanium	275

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TABLE XL

ESTIMATE OF UPPER TOLERANCE LIMITS FOR IMPURITIES IN ZIRCONIUM BASED ON
CORROSION TESTS IN HIGH TEMPERATURE WATER

<u>Impurity</u>	<u>Upper Limit, ppm</u>	<u>Impurity</u>	<u>Upper Limit, ppm</u>
H ₂	At least 1000	Ca	50
N ₂	50, lower if possible	Ti	80
O ₂	At least 200	Fe	850
C	400	Cd*	1
B*	1	Pb	20
Na	50	Cl	10
Mg	20	Ni	At least 750
Al	100	Cr	At least 500
Si	At least 800	W	500
P	50	Hf	No effect to 25,000

* Based on poisoning effect

H. EFFECT OF SURFACE FINISH

Generally ground surfaces are less corrosion resistant than machined surfaces, presumably because of the imbedded impurities from the grinding wheel. After studying various surface finishes, Battelle⁽⁴⁷⁾ concluded that the effect of surface condition can be very important and deceptive in the corrosion testing of zirconium. The most corrosion resistant finish was produced by clean cuts with sharp tools. Machining introduced a disturbed layer that extended 0.002-0.003 in. below the surface and nitrogen in the water vigorously attacked

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this layer. Neither the surface ground finish nor that produced by abrasion with hand papers was as resistant as lathe-turned finishes. Peening, wire brushing and vapour blasting produced surfaces subject to rapid corrosion^(42,47,49).

After many of the above surface preparations good corrosion resistance can be restored by a short pickle in a 50% HNO_3 -2% to 5% HF solution. Specimens should be pickled prior to corrosion testing, and material to be used under corrosive conditions should also be given this treatment. A recommended procedure is to degrease the material with some agent, such as trichlorethylene, pickle, wash in water, and dry prior to use.

I. EFFECT OF GALVANIC COUPLING

Battelle and MIT reported that zirconium with initially good corrosion resistance was not affected in water by coupling with stainless steel. After testing a zirconium -347SS couple for 250 hours in 600°F water, Argonne found the stainless was pitted over the surface while the zirconium showed some evidence of pitting along the edge of contact⁽⁴⁹⁾.

J. CREVICE EFFECTS

At Battelle, preselected zirconium samples were bent over a small radius until cracks developed in the outer surface and exposed to water at 660°F. One sample was tested under tension, while the other was tested "as bent". After two weeks exposure, white oxide appeared in the cracks of both samples, but further testing for three months gave no indication of more oxide formation than was observed at two weeks. Specimens with crevices as represented by tapered

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threaded joints made from zirconium corroded slightly after 6 weeks in 660°F water. No visible increase in oxide was apparent after an additional month's exposure⁽⁴⁹⁾. Crevice corrosion seemed to be a result of incomplete cleaning rather than a function of the crevices themselves.

Argonne found that mechanical removal of surface contaminants by polishing minimized crevice corrosion of zirconium⁽⁴¹⁾. Zirconium samples given two different surface treatments - 1) in the as-cut condition after sawing and 2) a polishing operation after sawing - were held in contact with each other with a film of water between the two faces. Combinations studied in 600°F degassed, distilled water were 1) both faces as cut, 2) both faces polished and 3) one face as cut, one face polished. Corrosion products were noted on the "as cut" faces but not on the polished; corrosion was essentially the same for test and control samples having corresponding surface treatments.

In addition to tests, the following observations have been noted⁽⁴¹⁾:

1. Dynamic and static corrosion tests of fuel plates at 550°F in contact with each other do not show corrosion at the contact areas.
2. In the screening test for the selection of corrosion resistant crystal bar zirconium, crevices are formed between bars in the autoclave. Crevice effects have not been observed in any screening test.
3. Routine production testing of crystal bar zirconium and fuel plates in stainless steel holders at temperatures of 500°F, 550°F and 600°F show no effect from the zirconium stainless steel crevice.

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4. An aluminum-zirconium couple formed by bolting an aluminum washer between a preselected corrosion resistant crystal bar zirconium bolt and nut showed no crevice effects at the threads after testing in 300°F water.

K. EFFECT OF COLD WORKING

Cold reductions up to 50% improved the corrosion resistance of arc-melted sponge zirconium when tested in 600° and 680° F water and in 750° F steam. The lowest weight gains as shown in Table XLI for 680° F were exhibited by the specimens reduced 10% to 20% (45).

TABLE XLI

EFFECT OF COLD WORK ON CORROSION OF ZIRCONIUM

% Reduction in Thickness	Wt. Gain mg/cm ² at Indicated Times in Days							
	7	14	21	28	42	56	84	112
0	20	15	20					
10	11	8	14	18	26	22	28	35
20	12	11	12	15	22	22		
30	7	12	19	11	27	18	35	
50	14	19	21	22				
70 *	21	50	136					

All samples were initially annealed at 900° C for one hour and then furnace cooled.

* Edge cracking observed.

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In some tests, cold work slightly improved the corrosion resistance of zirconium which was initially unsatisfactory but had little or no effect on material initially showing good corrosion behavior (49). Specimens of zirconium reduced up to 60% at 790° C and tested for 36 days in 750° F steam were not effected but rolling at 790° C to 955° C produced a detrimental effect. This was more pronounced at reductions of 50 to 60% than at lower reduction (47).

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II - ZIRCONIUM-TIN ALLOYS

Attention was drawn to tin as a beneficial alloying addition to zirconium by tests at BMI which showed that 10% tin increased remarkably the corrosion resistance of a grade of zirconium which otherwise would have been expected to have poor corrosion resistance. Subsequent tests have shown that tin can counteract the adverse effects of both nitrogen and carbon in sponge and poor quality crystal bar zirconium as well as other deleterious impurities such as titanium. In addition, tin strengthens zirconium.

A. EFFECT OF TIN ON SPONGE AND CRYSTAL BAR Zr

The results of tin additions to sponge and crystal bar zirconium are shown in Table XLII⁽⁴⁹⁾ and Figure 14.

The addition of 5% tin increased the corrosion resistance of sponge and poor quality crystal bar zirconium in 600° F water but did not improve good quality crystal bar. Alloys containing 10% tin did not show marked improvement over those containing 5% tin.

TABLE XLII

EFFECT OF TIN ON CORROSION RESISTANCE OF ZIRCONIUM IN 600° F WATER

(a) Arc-melted iodide Zr known to have good corrosion resistant properties		(b) Arc-melted and forged poor quality zirconium	
% Sn	Wt. Gain mg/cm ² 1300 hrs.	% Sn	Wt. Gain mg/cm ² 253 hrs.
0	0.11	0	Bad
1	0.12	1.01	Bad
5	0.11	2.98	0.18
10	0.16	4.85	0.15

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Figure 14

CORROSION BEHAVIOR OF ZIRCONIUM TIN ALLOYS IN WATER AT 600°F

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(c) Arc-melted Bureau of Mines Sponge (treated and outgassed)		(d) Arc-melted Bureau of Mines Sponge (untreated)	
<u>% Sn</u>	<u>Wt. Gain mg/cm² 1300 hrs.</u>	<u>% Sn</u>	<u>Wt. Gain mg/cm² 782 hrs.</u>
0	2.63	0	2.72
1	1.58	1	1.86
5	0.13	5	0.21
10	0.18	10	0.17

After one years exposure to 600 F water a 5% tin alloy made from poor quality crystal bar zirconium had a corrosion rate of 0.09 mg/cm²/mo. Tin-free and 1% tin alloys produced from untreated sponge failed between 2 and 3 weeks exposure (49).

B. EFFECT OF TIN ON NITROGEN

A study of the amount of nitrogen which can be tolerated for a given tin alloy was undertaken at MIT. Pure nitrogen gas was added to grade I crystal bar by diffusion at 1500-1600° C. After vacuum drip melting, tin was added and the ingots redripped five additional times. Some samples were 30% cold reduced followed by a two-hour anneal at 700° C to put them in a "standard metallurgical state". Corrosion rates for the specimens in 600° F water are shown in Table XLIII.

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TABLE XLIII

NITROGEN TOLERANCE VERSUS TIN CONTENT ON CORROSION
OF ZIRCONIUM IN 600° F WATER

Sample No.	ppm N ₂	% Sn	Corrosion Rate (mg/cm ² /mo)
877	1365	2.03-2.51	1.3
876	1156	.83-.86	32
921*	975	1.91-2.16	2.6
977*	970	1.65-3.14	3.5
920*	975	2.32-2.60	1.2
976*	990	2.62-3.12	Low
878	864	.30-.35	13
875	892	.43-.46	23
974*	900	1.73-2.14	1.5
918*	870	2.07-2.13	Negligible
975*	880	2.73-2.75	Low
893	906	2.83-2.96	.07
894	820	1.19-3.58	3.5
880	791	1.60-1.70	.53
972*	810	1.98-2.45	Low
973*	790	2.21-2.55	1.4
895	752	2.32-2.97	Negligible
879	676	.86-.88	5.6
919*	725	2.22-2.48	1.2
896	671	2.42-2.93	Negligible
881	427	.35-.36	2.2
883	368	2.40-2.41	Negligible
882	306	.72-.89	Negligible
870	197	.87-1.07	Negligible

*Cold rolled 30%, annealed 2 hours at 700° C.

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Although a regular series of tin alloys of an exact composition could not be produced by the drip melting method, from these and other tests estimates were made of the nitrogen tolerance for a given tin content. Limits are shown in Table XLIV ⁽⁵¹⁾. Roughly, each percent of tin will overcome the effects of 300 ppm of nitrogen.

TABLE XLIV

TOLERANCE LIMITS FOR NITROGEN IN Zr-Sn ALLOYS

<u>% Sn</u>	<u>Tolerance limit for N₂ in ppm</u>
0.0	60-100
0.5	200
1.0	300
2.0	600
2.5	700
3.0	800

C. EFFECT OF TIN ON CARBON

Although induction graphite melting is one of the best methods of producing massive zirconium, it was necessary to exclude this method because of carbon pickup with the resulting poor corrosion resistance in 600 F water. Alloying with tin will counteract the adverse effects of carbon as shown in Table XLV ⁽⁵²⁾. The sample with no tin corroded quite rapidly at 600° F, whereas at 450° F a sample of the same material exhibited good corrosion resistance for a long period of time. The addition of 1% tin caused a marked increase in the corrosion resistance of graphite melted zirconium.

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TABLE XLV

CORROSION OF GRAPHITE-MELTED EXTRUDED ZIRCONIUM-TIN
ALLOYS AT VARIOUS WATER TEMPERATURES

Sample	Analysis		350° F		450° F		600° F	
	% C	% Sn	Days	mg/cm ²	Days	mg/cm ²	Days	mg/cm ²
A	0.17	0.0	280	.05	250	wt.loss	18	.81
B	0.12	0.97	280	.03	298	.06	238	.24
C	0.19	2.43	280	.01	298	.03	238	.29
D	0.085	5.18	280	0	298	.03	238	1.06

MIT investigated the amount of carbon that could be tolerated for a given tin alloy. Table XLVI lists graphite melted tin alloys in order of increasing carbon content (52). It appears that for about 1-2.5 wt. % tin, the maximum carbon tolerance is 0.15-.16 wt. % carbon.

TABLE XLVI

CARBON TOLERANCE OF GRAPHITE-MELTED ZIRCONIUM-TIN
ALLOYS IN 600°F WATER (AS CAST)

No.	% C	% Sn	Time (days)	Wt. Gain (mg/cm ²)
1	0.054	2.51	196	0.27
2	0.070	2.49	196	.27
3	0.072	2.42	310	.27
4	0.079	2.5	281	.30
5	0.11	3.1	281	.57
6	0.12	2.23	309	.15
7	0.13	2.5	140	.49
8	0.14	2.8	281	.50
9	0.15	1.09	304	.43
10	0.15	2.72	223	.39
11	0.16	2.80	307	.45
12	0.17	1.99	7	1.28
13	0.17	2.84	97	.94
14	0.18	.96	28	.57
15	0.19	2.97	307	.56
16	0.23	.56	7	1.06
17	0.26	1.07	7	1.61

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Since carbide particles in zirconium are severely attacked during corrosion, extrusion would be expected to improve resistance to water by breaking up the continuity of the carbides. The effect of mechanical work on the corrosion resistance of graphite melted zirconium alloys is shown in Table XLVII. Two zirconium-nickel samples are included for comparison since several investigators have observed that Ni, Cr, and Sb, as well as tin are effective in overcoming the adverse effect of carbon. Even for non-alloyed zirconium, extrusion improved the corrosion resistance (52).

TABLE XLVII

EFFECT OF MECHANICAL WORKING ON THE CORROSION
RESISTANCE OF GRAPHITE MELTED ZIRCONIUM ALLOYS IN 600°F WATER

<u>No.</u>	<u>% C</u>	<u>% Alloy</u>	<u>As Cast</u>		<u>Extruded*</u>	
			<u>Time</u> <u>days</u>	<u>Wt. Gain</u> <u>mg/cm²</u>	<u>Time</u> <u>days</u>	<u>Wt. Gain</u> <u>mg/cm²</u>
1	.16	0	10	3.32	18	.51
2	.18	0.96 Sn	28	.57	280	.21
3	.20	0.55 Sn	7	1.40	63	1.49
4	.11	1.0 Ni	195	Wt. loss	334	.38
5	.26	0.51 Ni	44	Wt. loss	64	.50

* Reduction Ratio 16 to 1

E. MECHANISM OF PROTECTION BY TIN

The addition of tin to zirconium appears to permit growth of a thicker and more protective film. The reaction taking place during corrosion of zirconium can be shown by the equation $\text{Zr} + 2 \text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2 \text{H}_2$. Of the hydrogen evolved, 60% enters the metal in pure zirconium but only 30% enters a Zr-Sn alloy. Although zirconium exhibits good corrosion resistance to high

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temperature water, thermo-dynamically it is a most reactive metal. At 227°C (440°F) its oxidation by water is accompanied by a decrease of free energy of 187 K cals, whereas the figure for sodium - which reacts violently - is only 31 K cals. per mol. The corrosion resistance is due entirely to the formation of a protective film.

Chemical analysis indicates that tin in a Zr-5% Sn alloy is present in the oxide formed therefrom in nearly the same ratio, inferring that the stannic ion occupies zirconium ion lattice sites in the oxide. The ionic size ratios are favorable. Since tin in the oxide is not detected by X-ray diffraction, it indicates that the tin is in solid solution in the oxide, the Sn ⁴⁺ ion replacing the Zr ⁴⁺ ion in the oxide lattice.

The tin-free alloy is believed to produce inherently more permeable films, which are, however, susceptible to recrystallization depending on the impurities present. The tin may provide a better bond between the oxide and dissimilar phases such as nitrides and carbides so that cracking and devitrification are suppressed.

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III - ZIRCALOY-1

As a result of the erratic corrosion resistance of crystal bar zirconium, considerable research and development was directed toward the production of satisfactory alloys. Since sponge is approximately 1/2 the cost of crystal bar, the program was aimed at alloys using a sponge base.

Battelle Memorial Institute and Iowa State College found that up to 5% tin improved the corrosion resistance of sponge zirconium or off-grade crystal bar. A nominal composition of 2.5% tin in a sponge zirconium base resulted in the optimum corrosion and mechanical properties. This zirconium-2.5% tin alloy was called Zircaloy-1; its nominal composition is shown in Table XLVIII.

The effect exerted on sponge and good quality crystal bar zirconium by the addition of 2.5% tin is shown schematically in Figure 15 ⁽⁵³⁾. Tin improves the corrosion resistance of sponge and poor quality crystal bar but decreases the corrosion resistance of good quality crystal bar zirconium.

Zircaloy-1, like zirconium, is subject to "breakaway". For example, the corrosion of Zircaloy-1 in 680° F water proceeds at a low rate for a period of about 60 days at which time corrosion increases to a new and considerably higher rate. An adherent brown corrosion product formed in the latter period reaches thicknesses great enough to interfere seriously with heat transfer.

The corrosion behavior of Zircaloy-1 did not come up to expectations, for although it improved the corrosion resistance of the less expensive Kroll-process sponge zirconium by delaying breakaway time, it did not eliminate this flaking and spalling of the white oxide film. The corrosion behavior was also not as reproducible and predictable as desired.

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TABLE XLVIII

NOMINAL COMPOSITION OF ZIRCALOY-1

<u>Element</u>	<u>Percent</u>
Sn	2.2-2.8
Fe	0.04-0.08
Cr	0.015 max.
Ni	0.005 max.
N	0.006 max.
Bal	Sponge Zirconium

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Figure 15
CORROSION BEHAVIOR OF ZIRCONIUM ALLOYS

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IV - ZIRCALOY-2

In high temperature water and steam the addition of 0.1-0.5 wt. % Fe, Ni, or Cr to sponge zirconium delayed post breakaway corrosion. In ternary alloys, Fe, Ni or Cr substantially improved the corrosion resistance of Zr-Sn alloys. An alloy was eventually prepared having 1.5% Sn plus small amounts of Fe, Cr, and Ni in a sponge zirconium base. This alloy was called Zircaloy-2 and its nominal composition is shown in Table XLIX.

TABLE XLIX

NOMINAL COMPOSITION OF ZIRCALOY-2

<u>Element</u>	<u>Percentage</u>
Sn	1.3 - 1.6
Fe	0.09 - 0.14
Cr	0.07 - 0.11
Ni	0.04 - 0.06
N	0.006 max
Bal	Sponge Zirconium

Generally, this alloy is not effected as extensively by impurities and environment as zirconium or zircaloy-1. Mechanically, zircaloy-2 has more favorable characteristics and is therefore more suitable as a production material than either crystal bar or zircaloy-1. Zircaloy-2 is the alloy currently being used in the Mark II core as well as in other reactors.

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A. EFFECT OF CHEMICAL COMPOSITION

The corrosion resistance of Zircaloy-2 is primarily dependent on the total iron, nickel and chromium content within the combined element range of 0.20 to 0.34 percent. Corrosion rates decrease with increasing total alloy content in the above range.

1. Effect of Tin

Table L shows the alloys studied by Goldman and Thomas ⁽⁵⁴⁾ to determine the effect of tin content on Zircaloy-2 exposed to 680° F water and 750° F steam for extended periods of time. Weight gains are shown in Table LI and Figure 16. All alloys were made from the sand blend of sponge.

TABLE L
COMPOSITION, WEIGHT PERCENT

<u>Sample No.</u>	<u>Sn</u>	<u>Fe</u>	<u>Ni</u>	<u>Cr</u>	<u>N₂</u>	<u>Total Fe / Ni / Cr</u>
1	—	0.085	0.003	0.003	0.007	0.091
2	0.07	0.100	0.052	0.091	0.009	0.243
3	0.60	0.119	0.065	0.102	0.007	0.286
4	1.05	0.086	0.051	0.090	0.007	0.227
5	1.52	0.100	0.055	0.104	0.006	0.259

Analyzing this data results in the following:

- (1) Above a certain necessary minimum concentration of Fe, Ni, and Cr, at 680° F and 114 days the effect of tin content on weight gain is negligible.
- (2) In 750° steam, modified Zircaloy-2 containing 0.07% tin is slightly superior to other samples with higher tin contents.

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TABLE 51

WEIGHT GAIN DATA AT 680°F AND 750°F FOR MODIFIED ZIRCALOY-2 ALLOYS

(All Material in Hot Rolled Condition)

Weight Gains, mg/cm², 680°F,
at indicated times in days

Sample No.	% Sn	14	28	42	56	70	84	114
1	- -	white, discontinued						
2	0.07	.17	.19	.21	.24	.25	.34	.43
3	0.60	.19	.20	.23	.25	.28	.27	.33
4	1.05	.17	.20	.22	.24	.27	.27	.38
5	1.52	.17	.18	.19	.22	.26	.29	.33

Wt. Gains, mg/cm², 750°F at indicated days

Sample No.	3/4	3-3/4	10-3/4	17-3/4	24-3/4	31-3/4	45-3/4
1	.27	1.00	discontinued				
2	.17	.24	.33	.40	.42	.57	.62
3	.15	.22	.29	.37	.39	.46	.64
4	.14	.20	.32	.36	.38	.52	.64
5	.9	.23	.32	.39	.45	.57	.66

59-3/4	63-3/4	80-3/4	94-3/4	108-3/4	127
.66	.67	.82	.87	.90	.95
.77	.89	1.08	1.21	1.30	1.55
.84	.98	1.13	1.34	1.47	1.85
.79	.86	1.09	1.10	1.17	1.46

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Figure 16

EFFECT OF TIN ON CORROSION OF ZIRCALOY-2
EXPOSED TO 750°F STEAM, 1500 psi

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(3) The poorer corrosion resistance of the 1% tin alloy exposed to 750° F steam may be associated with the lower total iron, nickel and chromium content. From these and other tests, it was found that varying the tin content from 0 to 1.5% has little or no effect on the corrosion resistance in water of high quality sponge zirconium alloys containing 0.1% Fe, 0.1% Cr, and 0.05% Ni.

2. Effects of Iron, Nickel and Chromium

Later experiments were performed to study the relative effects of iron, nickel and chromium when added individually to a sponge zirconium base. Studies were also made to determine the relative effects when the elements were added individually and combined to a binary zirconium-tin alloy. These alloys are shown in Tables LII and LIII (54).

Corrosion data was obtained over extended time periods but no definite trend with any variations of individual iron, nickel or chromium was noticed. As shown in Figures 17 and 18, when weight gains for the samples in Table LII were plotted against the total iron, nickel and chromium contents, some correlation was obtained. After 14 days exposure to 680° F water, the total iron, nickel and chromium content had no apparent effect upon the weight gain. After 98 days, however, a minimum weight gain occurred in the vicinity of 0.3%. Similar trends resulted for alloys exposed to 750° F steam, except that the minimum weight gain appears after 12 days exposure.

No significant correlation between weight gain and iron content was apparent when ingots in Table LIII were tested. The comparison of weight gain and total iron, nickel and chromium content, as shown in Figure 19, follows

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the same trend as in Figures 17 and 18. The weight gain decreased slightly with increasing total iron, nickel and chromium contents in the narrow range (0.25 to 0.39%) represented.

TABLE LII

ZIRCALOY-2 WITH VARYING IRON, NICKEL AND CHROMIUM CONTENTS
(ALL CONTAIN 1.5% Sn)

Weight Percent of Element				
<u>Sample No.</u>	<u>Iron</u>	<u>Nickel</u>	<u>Chromium</u>	<u>Total (Fe / Ni / Cr)</u>
H-443	0.09	0.006	0.028	0.12
H-446	0.15	0.003	0.089	0.23
H-444	0.17	0.003	0.103	0.28
H-445	0.14	0.026	0.043	0.21
F-765	0.09	0.043	0.098	0.23
G-764	0.13	0.062	0.09	0.28
F-767	0.22	0.11	0.18	0.51
F-766	0.18	0.14	0.10	0.42
G-763	0.11	0.11	0.03	0.26

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Figure 17

THE EFFECT OF TOTAL IRON, NICKEL AND CHROMIUM CONTENT
ON THE CORROSION OF ZIRCALOY-2 IN STEAM
AT 750°F, 1500 psi

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Figure 18

THE EFFECT OF TOTAL IRON, NICKEL AND CHROMIUM CONTENT
ON THE CORROSION OF ZIRCALOY-2 IN 680°F WATER

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Figure 19

THE EFFECT OF TOTAL IRON, NICKEL AND CHROMIUM
ON THE CORROSION OF ZIRCALOY-2 IN
750°F STEAM, 1500 psi

TOTAL IRON NICKEL AND CHROMIUM, WEIGHT %

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TABLE LIII
ZIRCALOY-2 WITH VARYING IRON CONTENTS

<u>Ingot No.</u>	<u>Tin</u>	<u>Iron</u>	<u>Nickel</u>	<u>Chromium</u>	<u>Total (Fe / Ni / Cr)</u>
D-88	1.43	0.12	0.041	0.082	0.25
D-54	1.51	0.14	0.061	0.114	0.31
D-76	1.53	0.16	0.038	0.092	0.29
D-81	1.57	0.17	0.038	0.09	0.30
D-91	1.54	0.18	0.046	0.086	0.31
D-62	1.50	0.22	0.061	0.108	0.39

B. EFFECT OF TEMPERATURE

The corrosion rate of Zircaloy-2 increases with increasing temperatures as shown in Figure 20. The data was obtained in static autoclave tests using degassed, high purity water (54).

When the weight gains per unit area are plotted against time on logarithmic scales as in Figure 21, straight lines result having the general equation $W = Kt^n$ or $\log W = \log K + n \log t$, where:

W = weight gain per unit area

t = time

K = constant

n = constant

A straight line is obtained with the intercept equal to K and the slope equal to n. The rate law is parabolic if $n = 0.5$ and linear if $n = 1.0$. Constants K and n, which have been determined for Zircaloy-2 at four temperatures are shown in Table LIV.

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Figure 20

WEIGH GAIN TIME CURVES FOR THE CORROSION OF ZIRCALLOY-2
IN HIGH TEMPERATURE WATER AND STEAM

Number of Samples

550°F : 21
600°F : 9
680°F : 17-240
750°F : 2-151
850°F : 10

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Figure 21

EFFECT OF TEMPERATURE ON THE CORROSION OF ZIRCALLOY-2

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TABLE LIV

RATE CONSTANTS AND SLOPES FOR ZIRCALOY-2 AT VARIOUS TEMPERATURES

<u>Temp. °F</u>	<u>Medium</u>	<u>Pressure, psi</u>	<u>Equation (W in mg/cm², t in days)</u>
550	Water	750	$\log W = 0.24 \log t + 0.64$
600	Water	1500	$\log W = 0.27 \log t + 0.74$
680	Water	2700	$\log W = 0.38 \log t + 0.73$ up to t = 110 days
680	Water	2700	$W-33 = 0.4 (t-110)$ after t = 110 days
750	Steam	1500	$\log W = 0.40 \log t + 1.02$ up to 25 days
750	Steam	1500	$W-39 = 1.0 (t-25)$ after t = 25 days

With increasing temperatures, the slopes of the lines in Figure 20 also increase; e.g., from 0.24 at 550 F to 0.40 at 750 F (steam). The change in slope of the latter at about 25 days is presumed to correspond to the "breakaway" which had been observed in Zircaloy-1 at 7 days under the same test conditions. The post-breakaway rate of corrosion for Zircaloy-2 after 25 days is 0.30 mg/cm²/mo compared to 17.40 mg/cm²/mo for Zircaloy-1. No evidence of breakaway corrosion occurred for Zircaloy-2 in 550 or 600 F water.

Accelerated corrosion occurs in the 680 F water tests at about 110 days. After exposure time of 100 days at 680 F the data varies considerably, so that the breakaway time cannot be given very accurately. The rate of corrosion after breakaway is estimated to be 0.12 mg/cm²/mo.

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C. EFFECT OF HEAT TREATMENT

Results on Zircaloy-2 samples quenched or slow cooled from temperatures in the range 550 to 900° C generally do not indicate any marked dependence of corrosion resistance upon heat treatment as shown in Figure 22. A slow cool from 900 to 1000 C appears to be slightly beneficial to Zircaloy-2 and extremely advantageous to unalloyed sponge. Modifications of Zircaloy-2 with reduced tin contents react in much the same way. Quenching from above 1000 C, however, is particularly detrimental to Zircaloy-2 or modified Zircaloy-2 where the tin content is varied.

D. EFFECT OF PRESSURE

The effect of pressure on the corrosion of Zircaloy-2 is shown in Table LV (54). At 100 atmospheres the initial corrosion rate is higher than at one atmosphere, but the weight gain values approach each other after 756 hours (31.5 days).

TABLE LV

EFFECT OF PRESSURE OF ZIRCALOY-2 AT 750°F (STEAM)

<u>Time (hours)</u>	Weight gain, mg/cm ² <u>1 atm</u>	Weight gain, mg/cm ² <u>100 atm</u>
18	.02	.11
66	.03	.17
84	.05	.19
108	.08	.21
180	.16	.24
252	.21	.27
420	.22	.32
588	.26	.35
756	.33	.39
924	.43	.41

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Figure 22

EFFECT OF HEAT TREATMENT ON
CORROSION RESISTANCE OF ZIRCALOY-2

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E. EFFECT OF NITROGEN

Nitrogen in zirconium has been previously reported as being harmful to corrosion resistance when present in amounts above 0.006. Zircaloy-2 ingots, melted and fabricated at the Bureau of Mines, were nitrogenated to four levels by adding zirconium nitride to the sponge stage. Following alloying to the nominal composition of Zircaloy-2, these materials were heat treated prior to testing. Half of the samples were quenched from 800 C and the other half were slowly cooled from the same temperature. The results of the corrosion tests on these ingots in 680 F water and 750 steam are shown in Table LVI and Figure 23. The effect of nitrogen on Zircaloy-2 is shown in Figure 24 (43).

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TABLE LVI

CORROSION DATA FOR ZIRCALOY-2 CONTAINING VARIOUS

AMOUNTS OF NITROGEN
mg/cm²/day

<u>680°F Water</u>							
<u>% N₂</u>	<u>A*</u>			<u>B**</u>			
	<u>14</u>	<u>44</u>	<u>74 days</u>	<u>14</u>	<u>44</u>	<u>74 days</u>	
0.004	25	31	34	17	26	27	
0.008	16	25	31	13	28	44	
0.011	22	24	27	14	25	33	
0.025	21	29	42	22	26	47	

<u>750°F Steam</u>								
<u>%N₂</u>	<u>A*</u>							
	<u>3/4</u>	<u>1.5</u>	<u>8.5</u>	<u>15.5</u>	<u>22.2</u>	<u>29.5</u>	<u>36.5</u>	<u>43.5 days</u>
0.004	13	17	24	27	34	42	55	59
0.008	13	16	22	26	38	56	70	83
0.011	15	17	22	25	37	48	55	66
0.025	15	20	28	33	45	62	70	77
	<u>B**</u>							
	11	12	21	26	38	41	49	63
	10	10	24	30	39	58	74	85
	13	11	24	30	36	47	60	62
	19	22	33	35	56	63	75	90

A* - Water quench from 800°F
B** - Slow cool from 800°F

It would appear that the effect of heat treatment is negligible up to about 0.11% nitrogen. The deleterious effect of nitrogen is apparent with either heat treatment.

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Figure 23

THE EFFECT OF NITROGEN ON THE CORROSION RESISTANCE OF ZIRCALLOY-2

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Figure 24
EFFECT OF NITROGEN IN ZIRCALOY 2
750° F 1500psi

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V - SUMMARY

The corrosion behavior has been shown to be dependent on the presence of impurities such as nitrogen, carbon, titanium and aluminum. Alloying with tin, iron, nickel and chromium counteracts the adverse effect of the above impurities. Water composition, water velocity and stressing do not significantly effect the corrosion rate. Surface condition, temperature and cold working appear to determine the corrosion behavior, rates increasing with increasing surface roughness and temperature, but decreasing with 10-20% cold working. For a low enriched reactor of the APFR type in which the bulk water temperature is 500 F and the flow rate 6 fps, the corrosion rate of Zircaloy-2 would be approximately $0.10 \text{ mg/cm}^2/\text{mo.}$

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SECTION III

STAINLESS STEELS

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I - INTRODUCTION

Although the final selection of any material for a water cooled and moderated reactor depends on the cost, availability and ability to perform the job required, the corrosion resistance of the austenitic stainless steels has largely influenced their extensive use in reactor systems. Whereas various types of stainless, such as 304 and 347, have been used as structural material, only type 304 has been used as fuel element material for a power reactor (APPR-1)⁽⁵⁵⁾. This study only encompassed those types of stainless steel which appear promising as fuel element material.

Although the mechanism of corrosion is generally accepted as an electro-chemical process, it is affected by the continually changing equilibrium of the corrosion process and many other variables. Stainless steels have undergone considerable testing in high temperature aqueous mediums, but not much information has been furnished on the basic corrosion mechanism. Like most materials, the corrosion rate of stainless steel in water decreases with time. This phenomena may be attributed either to a reduction in surface area susceptible to attack or to the formation of films which protect the metal from the water. Figure 25 illustrates the decreasing corrosion rate with time for type 304 SS⁽⁵⁶⁾.

Stainless steels will generally either gain or lose weight, depending upon the composition of the corrosion medium. Although corrosion measurements may indicate a sudden loss in weight for a sample that has previously been gaining weight, this can be attributed to the erosion of the oxide; had this not occurred, the sample would have continued to gain weight. A weight gain

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Figure 25

CORROSION OF TYPE 304 SS IN HYDROGENATED WATER

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indicates the formation of a metallic compound, usually an oxide, whose composition is only partly that of the metal, possibly only 1/3. A weight decrease indicates that the total weight loss can be attributed to parent metal. The absolute weight change has been used by some investigators to determine the corrosion rate by plotting weight change vs time. The slope of the curve is the corrosion rate. This method assumes none of the oxide is lost to the water and no deposition of extraneous material from other sources occurs on the sample surface. To obtain accurate rates, however, the corrosion product must be stripped from the underlying metal. This metal can then be weighed to determine the actual corrosion rate.

Low flow rates such as 1 fps will remove little oxide whereas at higher flow rates, such as 30 fps, the fluid does its own descaling. For austenitic stainless steels, the corrosion is uniform; no intergranular corrosion of these steels in water has been noticed below 800 F (56).

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II - AUSTENITIC STAINLESS STEELS

The alloys of iron, chromium, and nickel are the most versatile non-precious corrosion resistant alloys. Some investigators believe the corrosion resistance of these alloys results from the presence of a thin oxide or hydrate film on the surface of the alloy which is stabilized by chromium; others believe that chromium shifts the location of iron in the EMF Series to make it more noble (57). It is generally agreed that passivation is not a continuous state and that it exists only in certain environments or under certain conditions. If passivity is due to a protective film, an environment that dissolves this film will obviously cause disintegration of the metal. Under many conditions, the range of passivity is broad, while in others the range is relatively narrow and may be destroyed by slight environmental changes.

Nickel is added to the chromium-iron alloys to render them austenitic because of useful mechanical properties and to expand the passivity limits of the chromium-irons. Better resistance to nonoxidizing media and to many neutral salt solutions is possessed by alloys having high nickel contents (58).

Additions of molybdenum to the austenitic chromium-nickel alloys tend to strengthen the passive film and improves the resistance of the alloys to pitting. However, additions of molybdenum tend to decrease the corrosion resistance of these alloys in strongly oxidizing environments.

Niobium (columbium), titanium, and vanadium are added to austenitic stainless alloys to combine with carbon, thus stabilizing the alloys against intergranular-type corrosion. Additions of these elements, however, frequently reduces the corrosion resistance of the alloys.

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In addition to the alloy compositions, changes in microstructure brought about by different heat treatments considerably affect the corrosion resistance of austenitic stainless alloys. Resistance is greatest when the carbon is completely in solution producing a homogeneous single-phase structure. Austenitic compositions exhibit a wide range of passivity when cooled rapidly from temperatures within the range 1850 to 2000° F. Rapid cooling from the heat-treating temperature is essential to prevent carbide precipitation from the austenitic solid solution.

A. EFFECT OF DISSOLVED GASES

The presence of dissolved gases such as oxygen, nitrogen, carbon dioxide, ammonia and hydrogen can affect the corrosiveness of water in a reactor system. The first three enter the water by absorption from the atmosphere. Both oxygen and hydrogen can be produced from dissociation of water by irradiation. Combination of hydrogen with nitrogen to produce ammonia can also occur under a radiation field. The effects of each of these gases on the corrosion of austenitic stainless steels will be discussed separately.

1. Effect of Oxygen

Since most of the corrosion products are oxides, dissolved oxygen would be suspected of increasing the corrosion rate. Although generally true, discrepancies do exist. Argonne (59) (60) has found that the presence of a small quantity of oxygen, such as less than 1 cc/liter, has a more corrosive effect than larger concentrations of oxygen. Since degassification will lead to a very low oxygen concentration, the higher and erratic corrosion rates in degassed water may be explainable on this basis.

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Investigations at Battelle⁽⁶¹⁾ indicated that 600 F degassed water and water containing 60 cc/liter of oxygen caused no crevice corrosion; when the oxygen level was raised to 300 cc/liter, however, seizure between couples was apparent.

2. Effect of Hydrogen

Since hydrogen is an effective depolarizing agent, its presence inhibits corrosion. In a reactor, irradiation tends to dissociate water; an excess of hydrogen tends to reverse the dissociation reaction, i.e.,

Since hydrogen is released in the corrosion process, it further helps to retard the reaction. The corrosion rates of 304 SS in hydrogenated water are shown in Figure 25.

The beneficial effect of hydrogen on corrosion rates compared to water containing dissolved oxygen is shown in Tables LVII and LVIII and Figures 26 and 28⁽⁵⁶⁾.

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TABLE LVII

EFFECT OF HYDROGEN AND OXYGEN ON THE CORROSION RATE
OF TYPE 304 AND 304L SS
H₂O AT 500° F

Loop Condition	Time (hrs)	304 SS		304L SS	
		30 fps	1 fps	30 fps	1 fps
0-1 cc O ₂ /1	500	0.08	0.24	-	0.12
	500	-	-	-	0.23
	1000	0.06	0.08	-	0.06
	1000	0.03	0.03	0.02	-
	1000	0.03	0.05	0.03	-
	1500	0.03	0.0	0.03	0.07
	1500	-	0.09	0.02	0.10
	1500	-	-	-	-
1-5 cc O ₂ /1	500	0.04	0	0.04	0.13
	500	0.02	0.12	-	-
	1000	-	-	-	0.05
	1500	0.03	-	-	-
25 cc H ₂ /1	500	0.04	0.02	0.01	0.03
	500	0.04	0.08	-	-
	1000	-	-	0.03	-
50 cc H ₂ /1	500	0	0	-	0
	1000	0.01	0.01	0.01	0.01
	1500	-	-	0.01	0
100 cc H ₂ /1	500	0.01	0.0	-	-
	500	0.02	0.02	-	-

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TABLE LVIII

AVERAGE CORROSION RATES IN VARIOUS ENVIRONMENTS
(mg/cm²/mo)

Water at 400° to 600° F

<u>Material</u>	<u>With Oxygen</u>		<u>With Hydrogen</u>		<u>Degassed</u>		<u>With Alkali</u>		<u>Irradiated</u>	
	<u>Samples</u>	<u>Rate</u>	<u>Samples</u>	<u>Rate</u>	<u>Samples</u>	<u>Rate</u>	<u>Samples</u>	<u>Rate</u>	<u>Samples</u>	<u>Rate</u>
304 SS	48	0.04	57	0.03	11	0.09	27	0.03	1	0.02
304L SS	32	0.07	27	0.03	6	0.07				
347 SS	44	0.09	78	0.04			3	0.04	14	0.08
316 SS	63	0.08	24	0.02	14	0.11	18	0.04		

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Figure 26 EFFECT OF HYDROGEN AND OXYGEN ON THE CORROSION RATE OF 304 SS

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3. Effect of Carbon Dioxide

Carbon dioxide dissolved in water will make it acidic as is illustrated in Table LIX (56). However, aside from the effects on specific resistivity of the water, carbonic acid has no appreciable effect on stainless steel (52).

TABLE LIX

EFFECT OF CARBON DIOXIDE IN WATER ON pH

<u>H₂CO₃</u> <u>Conc.</u>	<u>CO₂</u> <u>(ppm)</u>	<u>Hydrogen</u> <u>Ion</u>	<u>pH</u>
0.5 x 10 ⁻¹	2220	1.56 x 10 ⁻⁴	3.81
10 ⁻²	440	6.7 x 10 ⁻⁵	4.17
0.5 x 10 ⁻²	220	4.5 x 10 ⁻⁵	4.35
10 ⁻³	44	2.1 x 10 ⁻⁵	4.68
0.5 x 10 ⁻³	22	1.56 x 10 ⁻⁵	4.81
10 ⁻⁴	4.4	6.6 x 10 ⁻⁶	5.18
0.5 x 10 ⁻⁴	2.2	4.5 x 10 ⁻⁶	5.35
10 ⁻⁵	0.44	2.1 x 10 ⁻⁶	6.68
0	0	1.0 x 10 ⁻⁷	7.0

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4. Effect of Nitrogen

Besides introducing problems during shutdown as do other gases, nitrogen dissolved in the water is to a small extent converted to nitrates or nitric acid. Dissolved nitrogen will also combine with hydrogen, to a limited degree, forming ammonia. Like carbon dioxide, nitrogen may possibly effect the pH of the water as shown in Table LX (56). The austenitic stainless steels have fairly good resistance to corrosion by nitric acid in all concentrations and practically all temperatures due to the passivating action of nitric acid. Type 304 and 347 are commonly used for nitric acid up to the boiling point, while Types 309 and 310, stabilized with columbium, are better suited for temperatures above the boiling point. Unmodified chromium-nickel stainless steels, when they contain precipitated carbides resulting from sensitization in temperature range 800 - 1500° F, are susceptible to intergranular attack in nitric acid.

Molybdenum additions, as found in Types 316 and 317, do not improve resistance to corrosion by nitric acid (62)(63)(64)(65). The effect of nitric acid on Type 347 SS in hydrogenated water (100 cc/l H₂) at 500 F and flowing at 20 fps is shown in Table LXI (66)(67).

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TABLE IX

EFFECT OF NITRIC ACID IN WATER ON pH

<u>pH</u>	<u>Hydrogen (ppm)</u>	<u>Nitrate Ion (ppm)</u>
7	10^{-4}	0
6	10^{-3}	0.06
5	10^{-2}	0.62
4	10^{-1}	6.2
3	1	62

TABLE LXI

EFFECT OF ACID ON CORROSION OF TYPE 347 SS

<u>Material</u>	<u>Corrosion Rates (mg/cm²/mo)</u>	
	<u>Degassed</u>	<u>Not Degassed</u>
347 SS, as machined	-0.03	-0.03
347 SS, as machined	-0.02	-0.03
Passivated 30% HNO ₃	0	-0.03
Pickled 20% HNO ₃ , HF 5%	0.01	0.01
Pickled 10% H ₂ SO ₄	0	-0.01

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5. Effect of Ammonia

If ammonia is formed in the primary system of a water cooled and moderated reactor it might have a slight effect on the pH of the water. However, the 18-8 stainless steels have excellent resistance to corrosion by weak bases such as ammonium hydroxide ⁽⁶²⁾. A secondary effect of ammonia is its breakdown under irradiation as shown in Table LXII ⁽⁶⁸⁾.

TABLE LXII

<u>Conditions</u>	<u>O₂</u>	<u>H₂</u>	<u>N₂</u>	<u>CO₂</u>
1 molar solution at 7-1/2 hours	12%	63%	25%	
2980 cc/L at 120 hours	62 cc/L	2070 cc/L	842 cc/L	6.2 cc/L

B. EFFECT OF pH

Argonne dynamically tested Type 304 SS at various flow rates in 500 F water at pH's of 5.0 and 6.5. From Figure 27, a weight gain resulted in a pH of 6.5 and a weight loss at a pH of 5.0 with about equal weight change rates. Since these were unstripped weights, the higher flow rate (21 fps vs. 16 fps) at pH 5.0 may have descaled the oxide from the sample surface. At both pH's, however, the corrosion rates were approximately 0.05 mg/cm²/mo. ⁽²⁴⁾

In dynamic tests at Babcock and Wilcox, the corrosion rates of 304 SS were determined at a pH of 7 and 10 in oxygenated water. The latter pH was obtained by adding 106 mg. of NaOH to the water. The results are listed below in Table LXIII ⁽⁵⁶⁾.

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Figure 27

CORROSION OF AUSTENITIC STAINLESS STEEL
IN HYDROGENATED WATER

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TABLE LXIII

	<u>30 fps</u>		<u>1 fpm</u>	
	<u>1.7 cc O₂/l</u>	<u>2.1 cc O₂/l</u>	<u>1.7 cc O₂/l</u>	<u>2.1 cc O₂/l</u>
pH=7		-0.06		0.01
pH=10	-0.05		0.01	

Bettis used a lithium hydroxide regenerated ion exchanger (mixed bed ion exchange resin in the lithium-hydroxyl form instead of in the hydrogen-hydroxyl form) to have pH's of 10-10.5. This permits continuous purification of the water without continuous additions of base. The rates for machined 347 SS were 0.0 to -0.01 mg/cm²/mo at both a water velocity of 10 fps and 20 fps (56). Generally, however, the rates for austenitic stainless steels were not significantly lower than those obtained in neutral and acidic pH's (69).

C. EFFECT OF IRRADIATION

Generally, irradiation of Type 347 SS has increased the corrosion rate; no effect on 304 SS has been apparent. Type 347 S irradiated at ORNL for two weeks at 500 F, and 9 months at 300 - 400 F in an integrated flux of 1.5×10^{20} nvt corroded at a higher rate than unirradiated specimens as shown in Table LXIV (56).

TABLE LXIV

EFFECT OF IRRADIATION ON TYPE 347 SS

<u>Material</u>	<u>Corrosion Rate (mg/cm²/mo)</u>	
	<u>Irradiated</u>	<u>Non-Irradiated</u>
347 SS	0.014	0.009
347 SS	0.017	0.005

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D. EFFECT OF FLOW RATE

Although the effect of flow rate on austenitic stainless steels is not appreciable, the higher the water velocity past the sample surface, the greater will be the corrosion rate. This is illustrated in Table LXV and Figure 28. (42)(70)

TABLE LXV

CORROSION RATE VERSUS FLUID FLOW

<u>Material</u>	<u>pH-10</u>		<u>pH-7</u>	
	<u>30 fps</u>	<u>1 fpm</u>	<u>30 fps</u>	<u>1 fpm</u>
304 SS	-0.05	0.01	-0.06	0.01
304 SS Welded	-0.04	0.02	--	0.04
304 SS Sensitized at 1250 F	-0.04	-0.01	-0.06	0.04

From a tabulation of about 120 samples, analysis of the effect of flow upon corrosion of 304 SS with both oxygen and hydrogen dissolved in the water is shown in graphical form in Figure 28. The average rates obtained under all conditions is shown in Table LXVI.

A secondary effect of fluid flow is descaling the corrosion products from the metal surface and transporting them from one point in the system to another. This transfer not only bares the corroded surface for renewed attack, but it also can:

- (1) increase erosive potential of the water.
- (2) increase filtration problems
- (3) restrict flow by deposition of corrosion products in confined areas such as tubes and orifices.
- (4) deposit corrosion products throughout the system.

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Figure 28

CORROSION OF TYPE 304 SS vs FLUID FLOW

- - Oxygenated water
□ - Hydrogenated water

Subscripts Indicate Number of
Samples Averaged to Obtain Value

CORROSION RATE (mg/cm²-mo)

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FLOW (f.p.s.)

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TABLE LXVI

AVERAGE CORROSION RATES AT VARIOUS FLOW RATES
(mg/cm²/mo)

Water at 400° F to 600° F										
<u>Material</u>	<u>Fluid Flow</u> 0.01 fps		<u>Fluid Flow</u> 10 fps		<u>Fluid Flow</u> 20 fps		<u>Fluid Flow</u> 30 fps		<u>In Autoclave</u>	
	<u>Samples</u>	<u>Rate</u>	<u>Samples</u>	<u>Rate</u>	<u>Samples</u>	<u>Rate</u>	<u>Samples</u>	<u>Rate</u>	<u>Samples</u>	<u>Rate</u>
304 SS	46	0.03	11	0.03	12	0.04	52	0.05	19	0.02
304L SS	24	0.04					31	0.06		
347 SS		0.04	9	0.038	10	0.02	63	0.07	32	0.06
316 SS	43	0.03	33	0.03			49	0.12		

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Should deposition occur on heat transfer surfaces, the resulting scales would lower the heat transfer efficiency. If the particles are radioactive and deposition occurs, problems could arise if the material is deposited in unshielded areas.

E. EFFECT OF WATER PURITY

Although the corrosion products themselves are not readily ionized, the ions produced in conjunction with other ions in the water can increase the corrosion rate if they are cathodic to the metal. The anodic and cathodic reactions that can occur as discussed by Evans,⁽⁵⁷⁾ Uhlig,⁽⁵⁷⁾ Gates⁽⁷¹⁾ and others.

To reduce corrosion, the dissolved and suspended solids should be^{as low as} practical. This is illustrated in Tables LXVII and LXVIII. In each case a demineralizer was used in one of two similar loops to maintain the water at high purity.⁽⁵⁶⁾

TABLE LXVII

EFFECT OF ION EXCHANGER ON CORROSION AT ARGONNE

H₂O at 500 F

<u>Material</u>	<u>Without Ion Exchanger</u> <u>mg/cm²/mo</u>	<u>With Ion Exchanger</u> <u>mg/cm²/mo</u>
304	0.17	0.04
316	0.16	0.04

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TABLE LXVIII

EFFECT OF ION EXCHANGER ON CORROSION AT WAPD

H₂O at 500 F, 0.1 cc O₂, 1700 hours

<u>Sample No.</u>	<u>Circuit Without Ion Exchanger</u> <u>mg/cm²/mo</u>	<u>Circuit With Ion Exchanger</u> <u>mg/cm²/mo</u>
1	0.09	0.05
4	0.09	0.06
7	0.09	0.05
8	0.09	0.05
10	0.10	0.06

The effect of water purity on heat transfer can be illustrated by a test loop that maintained an overall heat transfer coefficient of 3,300 Btu/hr-ft²-F° using demineralized water. One day following discontinuance of demineralization, the coefficient was reduced to 2,850 Btu/hr-ft²-F°, and seven days later to 1,600 Btu/hr-ft²-F°.

F. EFFECT OF SURFACE FINISH

Generally, the finer the metal surface finish, the less it is subject to continued corrosion. A smooth surface offers less foothold for foreign materials and is less likely to form small galvanic cells. The aggravated corrosion of vapor blasted surfaces compared to machined surfaces can be seen in Table LXIX. Additional tests under the same conditions, but at 1 fpm showed similar results. (72) (56)

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TABLE LXIX

EFFECT OF SURFACE FINISH ON CORROSION
H₂O at 500 F, 500 hours

<u>Material</u>	<u>Time (hr)</u>	<u>Conditions</u>	<u>Corrosion Rate (mg/cm²/mo)</u>	
			<u>Machined</u>	<u>Vapor-Blasted</u>
347 TaCb	500	500 cc H ₂ /L	0.01	-0.13
347 TaCb	1000		0.00	-0.03
347 TaCb*	500	0.2 cc O ₂ /L	-0.41	-0.78
347 TaCb*	500	Degassed	-0.09	-0.33
347 TaCb*	1000	0.2 cc O ₂ /L	-0.05	-0.46
347 TaCb*	1000	2.0 cc O ₂ /L	0.00	0.01
347 TaCb*	1000	Degassed	-0.04	-0.17
347 TaCb*	1500	Degassed	-0.04	-0.13
316 SS	500	500 cc H ₂ /L	0.00	-0.02
316 SS	500	Degassed	-0.04	-0.35
304L SS	500	0.2 cc O ₂ /L	0.01	-0.75
304L SS	500	2.0 cc O ₂ /L	0.04	0.03
304L SS	500	500 cc H ₂ /L	-0.04	-0.08
* Welded				

Generally, surface treatments, such as Malcomizing or Scottsonizing, in which carburization is used to improve the hardness, increase the corrosion rates as shown in Table LXX⁽⁷⁰⁾. Overall average rates for various finishes are shown in Table LXXI; average rates for various treatments in Table LXXII.

TABLE LXX

EFFECT OF SURFACE TREATMENT ON CORROSION

<u>Material</u>	<u>Temp.</u>	<u>Time (hr)</u>	<u>Test Conditions</u>	<u>Corrosion Rate (mg/cm²/mo)</u>
304 SS Chromallized	500	400	30 cc O ₂ /L	-2.4
304 SS Malcomized	500	1857	30 cc O ₂ /L	-0.24 to 0.064
304 SS Malcomized	500	1450	30 cc O ₂ /L	0.048 to 0.41
304 SS Malcomized Ground and Polished	500	337	Degassed	0.50

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TABLE LXXI

AVERAGE CORROSION RATES FOR VARIOUS FINISHES

(mg/cm²/mo)

Water at 400° F to 600° F

<u>Material</u>	<u>Polished</u>		<u>Malcomized</u>		<u>Tensile 10,000 psi</u>		<u>Sensitized</u>	
	<u>Samples</u>	<u>Rate</u>	<u>Samples</u>	<u>Rate</u>	<u>Samples</u>	<u>Rate</u>	<u>Samples</u>	<u>Rate</u>
304 SS	8	0.01	8	0.19			12	0.05
304L SS			10	0.47	1	0.01		

AVERAGE CORROSION RATES AFTER VARIOUS TREATMENTS

(mg/cm²-mo)

Water at 400° F to 600° F

<u>Material</u>	<u>As Welded</u>		<u>Quenched at 1900°</u>		<u>Machined</u>		<u>Vapor-Blasted</u>	
	<u>Samples</u>	<u>Rate</u>	<u>Samples</u>	<u>Rate</u>	<u>Samples</u>	<u>Rate</u>	<u>Samples</u>	<u>Rate</u>
304 SS	20	0.03	10	0.02	12	0.06		
304L SS	3	0.05					10	0.17
347 SS	28	0.17	27	0.07	44	0.54	5	0.15
316 SS	14	0.05	12	0.04	4	0.01	20	0.21

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III - MARTENSITIC STAINLESS STEELS TYPE 410 AND 440C

The hardenable chromium steels are affected by the same factors, such as dissolved gases, water velocity and surface finish, as are the chromium-nickel steels and in much the same way. Comparing the corrosion behavior of Types 410 and 440C with Type 304 stainless steels, the average rates for 440C were about 10 times higher and those for 410 about 15 times as great as for 304. This is illustrated in Tables LXXIII-LXXVII, where 410 and/or 440C martensitic stainless steels are compared with austenitic 304 and/or 347 under various conditions⁽⁵⁶⁾.

TABLE LXXIII

EFFECT OF OXYGEN ON CREVICE CORROSION

300 cc O₂/l

410 SS	vs	410 SS	Severe seizure
430 SS	vs	430 SS	Severe seizure
347 SS	vs	347 SS	Slight seizure

TABLE LXXIV

EFFECT OF HYDROGEN ON CREVICE CORROSION

385 cc H₂/l

410 SS	vs	410 SS	No seizure
430 SS	vs	430 SS	No seizure
347 SS	vs	347 SS	No seizure

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TABLE LXXV

EFFECT OF FLUID FLOW ON CORROSION

H₂O at 500° F

<u>Material</u>	Corrosion Rate (mg/cm ² /mo)			
	pH-10		pH-7	
	<u>30 fps</u>	<u>1 fpm</u>	<u>30 fps</u>	<u>1 fpm</u>
304 SS	0.05	0.01	0.06	0.01
440C SS	0.17		0.09	

TABLE LXXVI

EFFECT OF NaOH ON CORROSION

mg/cm²/mo

<u>Material</u>	30 fps	
	pH-10	pH-7
	<u>1.7 cc O₂/l</u>	<u>2.1 cc O₂/l</u>
304 SS	0.05	0.06
440C SS	0.17	0.09

TABLE LXXVII

EFFECT OF L₁OH ON CREVICE CORROSION

H₂O at 600° F, 300 cc O₂/l

<u>Couple</u>	<u>Clearance mils</u>	No L ₁ OH Seizure		With L ₁ OH (20 ppm) Seizure	
		<u>2 wk.</u>	<u>6 wk.</u>	<u>2 wk.</u>	<u>8 wk.</u>
410 SS vs 410 SS	0.5	Severe	Severe	None	Severe
430 SS vs 430 SS	0.5	Slight	Severe	None	Severe
347 SS vs 347 SS	0.5	None	None	None	None

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IV - SUMMARY

The effect of various environments, flow rates, surface finishes, etc. has been discussed for representative austenitic and martensitic stainless steels. The grand average corrosion rate for the types of stainless steels covered are listed in Table LXXVIII.

TABLE LXXVIII

<u>Material</u>	<u>No. of Samples Averaged</u>	<u>Corrosion Rate (mg/cm²/mo)</u>
304 SS	116	0.04
304L SS	66	0.05
347 SS	122	0.05
316 SS	101	0.07
440C SS	46	0.45
410 SS	37	0.60

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CONCLUSIONS

A survey has been completed on the corrosion behavior of three metals-aluminum alloys, zirconium alloys and stainless steels - for use as fuel element material in a Low Enriched Power Reactor. Table LXXIX lists the expected corrosion rate of the most applicable alloy from each group under the following operating conditions:

1. Temperatures of 450 - 500 F
2. Pressures of 1200 to 1500 psi
3. Deoxygenated Water
4. Flow Velocities of 5-7 fps
5. pH of about 6 to 7.5

TABLE LXXIX

EXPECTED CORROSION RATES FOR FUEL ELEMENT MATERIALS INVESTIGATED

<u>Material</u>	<u>Average Corrosion Rates</u> <u>mg/cm²/mo</u>	<u>Maximum Corrosion Rates</u> <u>mg/cm²/mo</u>
Type 304 SS	0.04	0.10
Zircaloy-2	0.05	0.15
M-388	1.1	2.9

Zircaloy-2 and Type 304 stainless steel have been used as fuel element material under the above conditions. M-388, a nominal 1% nickel in a 2S base, is the most promising aluminum alloy available today. This alloy is being used as fuel element material in the Argonne Low Power Reactor and several charges of slugs jacketed with M-388 have been in-pile tested by Hanford. An aluminum 6% copper alloy X-2219, has approximately the same

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corrosion rates under similar conditions, plus increased structural strength. However, for reactor applications, the additional alloy percentage is disadvantageous.

The corrosion rate of stainless steel and zirconium is not appreciably affected by temperature changes in the range of 450 to 600° F. With aluminum, corrosion rates increase with increasing temperatures. The temperature effect is inter-related with pH effect and the pH of "minimum" attack decreases with increasing temperatures.

Corrosion rates for austenitic stainless steel and aluminum are less in hydrogenated systems, aluminum being adversely effected by oxygen at elevated temperatures. The corrosion resistance of zirconium and its alloys is apparently increased in oxygenated systems and decreased in hydrogenated systems.

Slightly alkaline conditions are often useful in reducing the corrosion rates of steels and ferrous alloys; slightly acid conditions are useful in controlling the corrosion of aluminum and aluminum alloys. The corrosion resistance of zirconium and its alloys does not seem to be appreciably effected in the pH range of 5 - 9.

The corrosion resistance of all metals studied appeared to improve with increasing water purity. However, sufficient data on this subject is not available to specify optimum operating water conditions. General practice is to specify the highest purity water.

Contacts between any two metals widely separated in the EMF series and which do not build up protective films of high electrical resistance should be avoided. Such contacts will increase the tendency of the active metal to

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corrode. A corroding bi-metallic couple in an aqueous system is affected by three resistances; namely, anodic, cathodic and solution resistances. Any process which will increase these resistances will reduce corrosion. Anodic resistances may be increased by film build-up, and the solution resistance may be increased by the use of high purity water. Extensive galvanic corrosion which might otherwise be introduced by couples or crevices can thus be eliminated or significantly decreased. No appreciable galvanic effect was noted for zirconium or stainless steel and only a few instances were found for stainless steel-aluminum couples in high purity water.

The rate of flow is important in determining the amount of corrosion product deposition. Heaviest deposition at 500° F usually occurs at velocities less than 2 ft/sec. The corrosion rates of the metals studied increased slightly with increasing flow rates, but did not vary appreciable with velocities below 15 fps.

Either cold rolling or annealing decreases the corrosion resistance of aluminum whereas zirconium exhibits slightly increased resistance after cold working. Heat treating or cold forming operations generally do not affect the corrosion resistances of the 300 series stainless steels in high temperature water; the 400 series show slightly improved behavior in their hardened condition.

A high temperature corrosion inhibitor to be used in a reactor system should meet the following specifications: (1) the inhibitor will not decompose under irradiation and (2) the inhibitor will either not become excessively radioactive or will have a short half life so as not to impose

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serious purification and waste disposal problems. The first requirement excludes most organic corrosion inhibitors, the second excludes many conventional inorganic inhibitors.

The role of hydrogen or oxygen as corrosion inhibitors has been discussed. Many other additions which show inhibitive tendencies on stainless steel have been tested. These include sodium hydroxide, lithium hydroxide, hydrazine, morpholine, cyclohexylamine, sodium diphosphate, silicon dioxide, pertechnetate, zinc dioxide and germanium dioxide. Inhibitors beside hydrogen have also been evaluated for use in aluminum and zirconium systems at elevated temperatures but have not shown improvement in corrosion resistance.

The use of an aluminum alloy may prove advantageous from overall economic consideration, and would very markedly reduce the cost and complexity of fuel reprocessing systems. Although the data on aluminum looks encouraging, before reactor applications can be definitely recommended, several aspects of the corrosion behavior of M-388 need further investigation.

The effect of water purity on erosion, corrosion, differential potential cells and ionization would aid in understanding the mechanism of corrosion as well as provide information on which reactor water specifications could be based. In this respect, information is very meager on the relationship between suspended solids concentration and corrosion rates. Activation analysis in conjunction with dynamic testing might furnish useful information on the mechanism of corrosion along with determining the effect and distribution of trace impurities.

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Nickel plated aluminum has shown low corrosion rates in high temperature water but further dynamic testing is required to determine long-time rates. Nickel plating M-388 would lower the position of the aluminum alloy in the EMF series, reducing the differential between the alloy and passivated stainless steel and minimizing galvanic attack. Considerable research and development is needed on this subject.

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