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A MECHANISM FOR STRESS CORROSION CRACKING OF STAINLESS STEEL IN REACTOR SYSTEMS

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A MECHANISM FOR STRESS CORROSION CRACKING OF STAINLESS STEEL IN REACTOR SYSTEMS

by

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Approved by

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ABSTRACT

was developed that could explain [illegible] cracking

A mechanism ~~for~~ Chloride stress corrosion cracking of Type 304 stainless steel that has been sensitized, pickled, and dry ground, was shown to involve the chloride-bearing alumina present in the moderator-coolant system of Savannah River reactors. Chloride is absorbed by the alumina during its formation on hot fuel cladding; iron, an impurity in the cladding, greatly enhances chloride absorption. Alumina spalls and is transported by the coolant to the stainless steel surfaces. Chloride is released from the alumina by the acidic reaction at anodic sites on the steel. The negative chloride ion is attracted to the positive anodic site and initiates stress corrosion cracking.

Cracking of susceptible stainless steel by this mechanism can be reduced by:

- Controlling coolant pH (pD) between 5.0 and 5.2 to prevent general release of chloride.
- Avoiding addition of chlorides and chlorinated hydrocarbons to the reactor.
- Blocking anodic sites by inhibitors or by changing the potential of the stainless steel.

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INTRODUCTION

Several stress corrosion cracks have occurred in the Type 304 stainless steel cooling systems of Savannah River reactors: the first one after five years operation and subsequent ones at irregular intervals. Inspection of the cracks revealed intergranular corrosion confined to areas severely sensitized* by hot-forming and pickling operations during reactor construction.[1-3] Cracking was unexpected because the heavy water used as coolant and neutron moderator is very pure; conductivity is typically 3 micromhos/cm. The ionic content (0.5 ppm NO_3^-, 0.04 ppm $SO_4^=$, 0.02 ppm Cl^-) is generally considered noncorrosive to Type 304 stainless steel, even in the sensitized condition.[1]

Prevention of cracking is important to maintain continuity of reactor operation, eliminate expensive repairs, and minimize heavy water losses.

Chloride-bearing alumina from corroded aluminum reactor components has been implicated[1] in the cracking process. The cracking was observed to have both trans- and intergranular characteristics, but the mechanism was not known. The work reported here was designed to investigate the mechanisms by which the chloride-bearing alumina might cause stress corrosion-cracking.

Oxygen increases the sensivity of chloride stress corrosion cracking of stainless steel or lowers the chloride content necessary for cracking.[4,5] Oxygen also contributes to intergranular stress corrosion cracking of corrosion resistant steel above about ∿250°C in water at pH 10 with low oxygen content (∿0.1 ppm) or in neutral water with a high oxygen content (100 ppm).[6] These effects have been reviewed critically,[5] but were not evaluated in this study.

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* "Sensitized" is defined as heated in the range of 540-870°C, which precipitates chromium carbides in grain boundaries of the metal. In this condition, the material is very susceptible to intergranular corrosion.

SUMMARY

Three types of crystalline alumina were identified in the reactor system: $\alpha Al_2O_3 \cdot D_2O$ (Böhmite), $\alpha Al_2O_3 \cdot 3D_2O$ (Gibbsite), and $\beta Al_2O_3 \cdot 3D_2O$ (Bayerite). The α monohydrate and β trihydrate, which form on the aluminum-clad fuel elements and aluminum housings, spall and become suspended in the moderator as β trihydrate through stresses induced by the conversion from α monohydrate to β trihydrate and from thermal shock due to reactor shutdown and startup. The very finely divided turbidity is transported by the moderator and electrophoretically deposited on the stainless steel components where conversion to α trihydrate occurs. Turbidity sometimes contains high concentrations of α trihydrate due to erosion of deposits on the stainless steel by hydraulic upset of the cooling system.

Alumina absorbs chloride during oxide growth on aluminum surfaces. Very little chloride is absorbed on crystalline alumina. Iron present as an impurity in the aluminum is the primary contributor to chloride absorption during corrosion film growth. Silicon, also present as an impurity in the aluminum, is the primary contributor to rapid growth of the corrosion film.

A change in pH is the only effective mechanism for releasing absorbed chloride from alumina under typical reactor operating conditions. Stainless steel cracking observed in sensitized, pickled, and ground areas is indicated to be due to deposition of chloride-bearing alumina at anodic areas that are typically acidic. The negatively charged chloride is released and attracted to these positively charged areas to initiate the stress corrosion cracking sequence.

Stainless steel cracking that is caused by chloride-bearing alumina can be reduced by several methods. Maintaining the coolant pH (pD) between 5.0 and 5.2 reduces the general release of chlorides. Every effort should be made to prevent accidental addition of chloride to the reactor. Chlorinated hydrocarbons, which typically chemisorb on alumina, should not be used for degreasing when other reagents will serve equally well. The anodic sites where the cracks initiate might be blocked through the use of inhibitors or be inactivated by changing the stainless steel potential.

DISCUSSION

DESCRIPTION OF REACTOR COOLING SYSTEM

The nuclear reactors at Savannah River are constructed primarily of as-welded 304 stainless steel, small portions of which were severely sensitized by hot-forming operations during fabrication. The reactor vessel is a large cylindrical tank that contains the aluminum-clad nuclear fuel elements. Heavy water, the coolant and neutron moderator, circulates through the reactor vessel and fuel elements, and is discharged through six nozzles symmetrically spaced around the bottom of the tank. Large pumps circulate the heavy water through heat exchangers and back to a plenum in the top of the reactor vessel. Several side streams are taken from the main heavy water stream. One of these flows through an ion exchange resin bed for purification. A simplified schematic of the system is shown in Figure 1.

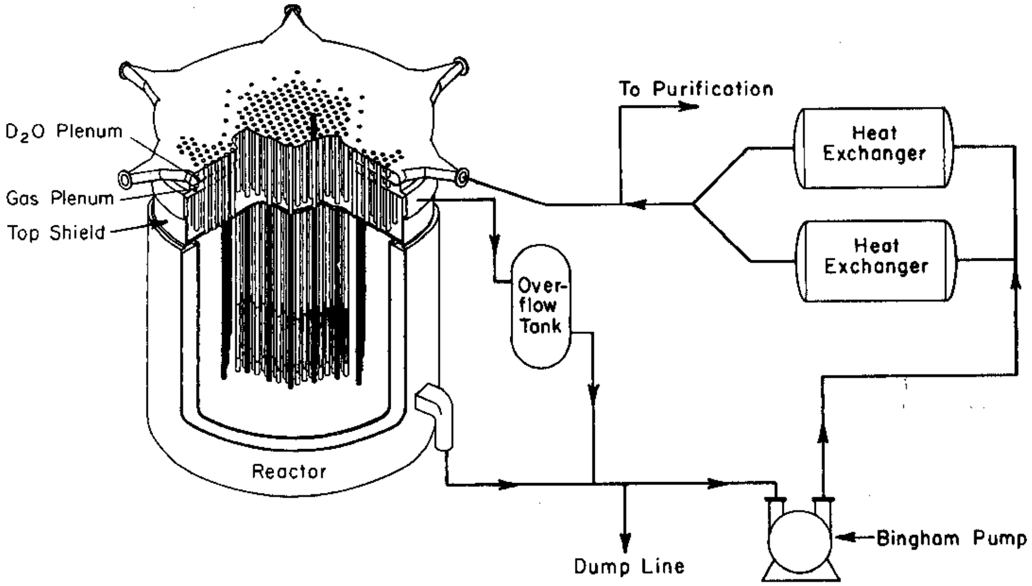

FIG. 1 SIMPLIFIED SCHEMATIC OF SRP NUCLEAR REACTOR

Mixed inter- and transgranular cracking, a variety of chloride stress corrosion, has occurred in several tank outlet nozzles and pump discharge lines. Relatively few cracks have occurred; the first one after more than five years of operation and subsequent ones at irregular intervals.

Films of alumina, formed by corrosion of aluminum-clad fuel elements, are deposited in portions of the reactor system. Analyses of the alumina deposits show chloride concentrations ranging from 10-10,000 ppm (0.001-1 wt %).

CHARACTERIZATION OF REACTOR DEPOSITS

Specimens of alumina were collected from the reactor system at several different locations. Scrapings were obtained from the 1) pump impellers and housings, 2) heat exchangers, 3) fuel cladding, and 4) various portions of piping. Moderator turbidity composed of finely divided alumina was trapped in the ion exchange resin bed and was also examined. Table I shows the various types of alumina found in the reactor system.

TABLE I

Aluminas Formed in Savannah River Reactor Systems

Formula	Structure, Crystal Class	Common Name	Principal Location
$\alpha Al_2O_3 \cdot D_2O$	AlO(OD) - orthorhombic	Böhmite	Fuel cladding
$\alpha Al_2O_3 \cdot 3D_2O$	$Al(OD)_3$ - monoclinic	Gibbsite	Steel surfaces
$\beta Al_2O_3 \cdot 3D_2O$	$Al(OD)_3$ - monoclinic	Bayerite	Moderator turbidity

The major quantity of alumina within the reactor at any given time is the $\alpha Al_2O_3 \cdot 3D_2O$ deposited on the stainless steel components. Typical analyses of deposits removed from the reactor tank outlet are shown in Table II. Typical deposits are tan, not white as would be expected for pure alumina.

TABLE II

Analyses of Alumina Adhering to Stainless Steel

Analysis Method	Determination	Amount
X-ray diffraction	$\alpha Al_2O_3 \cdot 3D_2O$	Major
Gamma pulse height	$^{95}Zr-^{95}Nb$	Major
	^{51}Cr	Major
	^{60}Co	Minor
Neutron activation	Cl	10-10,000 ppm
Emission spectroscopy	Al	>10 wt %
	Fe	5
	Cr	2
	Mn	1
	Ni	1
	Si	1
	Mg	0.5
	Ba, Ca, Cu, Sn, Ti	≤0.1

Although the major component of the scrapings is alumina, many impurities were identified by emission spectroscopy. Part of the iron, nickel, and silicon is from aluminum alloys, but most is probably from steel corrosion. The chromium and manganese are from steel corrosion; the magnesium is from aluminum corrosion.

ALUMINA FORMATION, TRANSPORT, AND DEPOSITION

The consistent identification of $\alpha Al_2O_3 \cdot 3D_2O$ as the major constituent in alumina deposits on stainless steel initially appeared to be anomalous. The α trihydrate is normally synthesized by aging hydrated aluminum oxide in solutions at pH 10 or by precipitating AlO_2^- at pH 9 or greater. The coolant is held at pD 5; therefore, the direct formation of α trihydrate is unlikely because of the small quantity of AlO_2^- ion and the large quantity of Al^{3+} ($Al^{3+}/AlO_2^- = 100/1$). The anticipated products at pH 5 would be $\beta Al_2O_3 \cdot 3D_2O$ below 80°C and $\alpha Al_2O_3 \cdot D_2O$ above 80°C, due to crystallization of amorphous $Al(OD)_3 \cdot xD_2O$.

After several attempts, the anomalous α trihydrate was synthesized by an indirect route; similar reactions would be expected during fabrication and irradiation of aluminum-clad nuclear fuels. Type 1100 aluminum was amalgamated to make it susceptible to corrosion at 25°C in water. The water was adjusted to pH 5 and readjusted daily throughout the experimental period during which the effects of increasing the temperature and of the addition of CO_2 were explored. The following transitions were observed by X-ray diffraction.

$$Al + (x+3)H_2O \xrightarrow[48\ hr]{25°C} Al(OH)_3 \cdot xH_2O + 3/2\ H_2 \tag{1}$$

$$2Al(OH)_3 \xrightarrow[6\ hr]{100°C} \alpha Al_2O_3 \cdot H_2O + 2H_2O \tag{2}$$

$$\alpha Al_2O_3 \cdot H_2O + 2H_2O \xrightarrow[500\ hr]{100°C\ +\ CO_2} \beta Al_2O_3 \cdot 3H_2O \tag{3}$$

$$\beta Al_2O_3 \cdot 3H_2O \xrightarrow[500\ hr]{100°C\ +\ CO_2} \alpha Al_2O_3 \cdot 3H_2O + \beta Al_2O_3 \cdot 3H_2O \tag{4}$$

Reaction 1 can occur in moist air and in water below 80°C. Reaction 2 occurs above 80°C. Reaction 3 could occur during reactor operation. Carbon dioxide was added during Reaction 3 because this gas had been used during reactor startup to maintain moderator pH (pD). Reaction 4, the transition from the β to α trihydrate, is not expected to occur rapidly. Calculated ΔF° values are -552 kcal for the formation of the β trihydrate and -555 kcal for α trihydrate.[7] These values indicate that Reaction 4 is slow even at elevated temperature. In fact the reaction was not observed during 10 years in a sealed sample in pure water at 25°C.[8]

The temperature and pH and the presence of CO_2 probably account for the formation of the α trihydrate in a relatively short time in these tests. The tests were designed to simulate reactor conditions with the exception of the neutron flux.

Some of the solid material that causes turbidity in the moderator was separated from ion exchange resin and was shown to be mainly $\beta Al_2O_3 \cdot 3D_2O$ containing 360 ppm Cl (Figure 2).

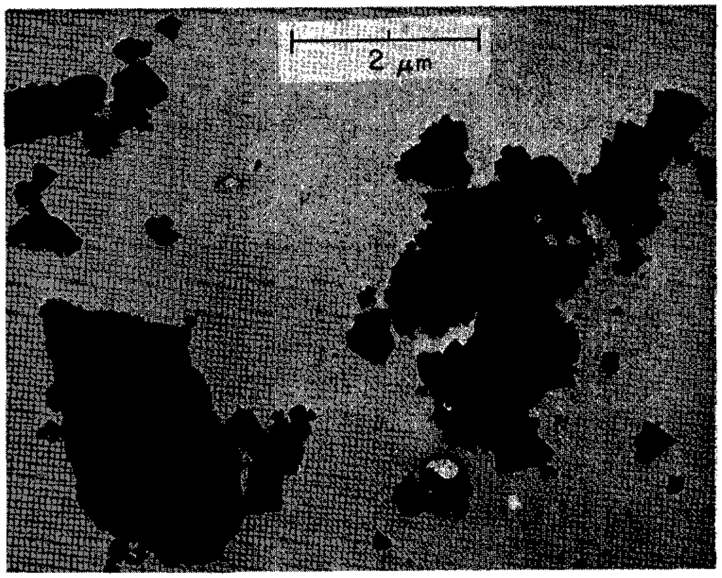

FIG. 2 TURBIDITY FROM ION EXCHANGE COLUMN

From the observed crystalline forms in the reactor system and the synthesis of $\beta Al_2O_3 \cdot 3H_2O$ in the laboratory, the deposition of alumina on stainless steel most logically follows the pattern:

1. Aluminum corrodes at low temperature to form $Al(OD)_3 \cdot xD_2O$ which converts to $\alpha Al_2O_3 \cdot D_2O$ during reactor startup or forms $\alpha Al_2O_3 \cdot D_2O$ directly during reactor operation.
2. $\alpha Al_2O_3 \cdot D_2O$ on the fuel hydrates to $\beta Al_2O_3 \cdot 3D_2O$ and then spalls because of stresses due to recrystallization from orthorhombic to monoclinic.
3. $\beta Al_2O_3 \cdot 3D_2O$, the main oxide present in turbidity as minute particles or agglomerates, is transported throughout the system.
4. The minute particles (<1 µm, Figure 2) electrophoretically deposit on the steel and gradually transform from β to $\alpha Al_2O_3 \cdot 3D_2O$.

Step 2 assumes that thermal shock has not occurred to remove protective aluminum oxide. Thermal shock sometimes occurs in reactor operation and accounts for the mixture of α monohydrate and β trihydrate found in turbidity. The presence of α trihydrate in turbidity is due to removal of the electrophoretic deposit by erosion or hydraulic upset.

CHLORIDE ABSORPTION BY ALUMINA

Alumina from Pure Aluminum and Commercial Alloys

Chloride was not absorbed by well-crystallized alumina suspended in water. As described in the Appendix, a suspension of amorphous $Al(OH)_3 \cdot xH_2O$ was produced by immersing an amalgamated aluminum surface in water at 25°C. After 8 days at pH 5, a well-crystallized $\beta Al_2O_3 \cdot 3H_2O$ had formed in the solution. At 100°C, amorphous $Al(OH)_3 \cdot xH_2O$ was again the initial product, but after about 4 hours the crystalline form was $\alpha Al_2O_3 \cdot H_2O$. Little chloride adsorption was observed either at 25 or 100°C when these crystallized products were added to pH 5 solutions containing $^{36}Cl^-$ as part of 1.5 ppm Cl^-. After 17 days the experiment was discontinued.

On the other hand chloride was absorbed on alumina as it was formed at a corroding surface. The aluminum was not amalgamated in this case, and a decrease in the radioactivity of the solution compared to a blank solution indicated adsorption of chloride. After 17 days a direct counting of the aluminum surface verified that the chloride had actually been absorbed in the oxide.

Table III compares the quantity of chloride absorbed by both particulate alumina and aluminum surfaces. These data suggest that 1) the absorption of chloride is high on oxidizing metal surfaces, 2) absorption occurs during the initial stages of film formation, and 3) absorption is not due to an alloying agent (Ni) but to an impurity in the aluminum. Deposition of chloride ions on selective locations, believed to be impurity sites, have been reported to occur in anodizing solutions.[9] Table III also shows that particulate alumina is a very poor absorber of chloride compared to a growing film of alumina. Even though the molar ratio of Al/Cl was 1000:1 in the particulate suspensions, little chloride was absorbed at 25 or 100°C. Impure alumina from 1100 alloy absorbed more chloride than pure alumina, but even these concentrations of chloride in alumina were low compared to concentrations found in the reactor system.

TABLE III

Absorption of Chloride by Alumina

Material[a]	Temp, °C	Absorbed Chloride, ppm
Particulate Alumina		
$\alpha Al_2O_3 \cdot H_2O$ - High purity aluminum	100	<0.2[b]
$\beta Al_2O_3 \cdot 3H_2O$ - High purity aluminum	25	<0.2[b]
$\alpha Al_2O_3 \cdot H_2O$ - 1100 aluminum	100	1
Corrosion Film on Aluminum Surfaces		
High purity aluminum	100	16
1100 aluminum	100	100
X8001 aluminum	100	100

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[a] High purity: 99.9995+% Al
1100: ⩾99.0% Al,<1.0% Si + Fe,<0.2% Cu,<0.1% Zn,<0.5% Mn
8001: 1100 Al + 0.9 to 1.1% Ni

[b] Lower limit of detection.

To verify that nickel was not the cause of chloride sorption, two specimens (one of 1100 Al and one of 8001) were oxidized in water for 10 days. The pH was held at 5, the temperature at 100°C, and the concentration at 1.5 ppm of Cl^- containing $^{36}Cl^-$. The oxide was 1.2 μm thick and had absorbed 6-8 x 10^{-8} g Cl^-/cm^2 in both cases. Autoradiographs of the X8001 alloy showed that chloride absorption was generally uniform and could not be ascribed to the relatively large particles of the nickel-rich phase (Figure 3).

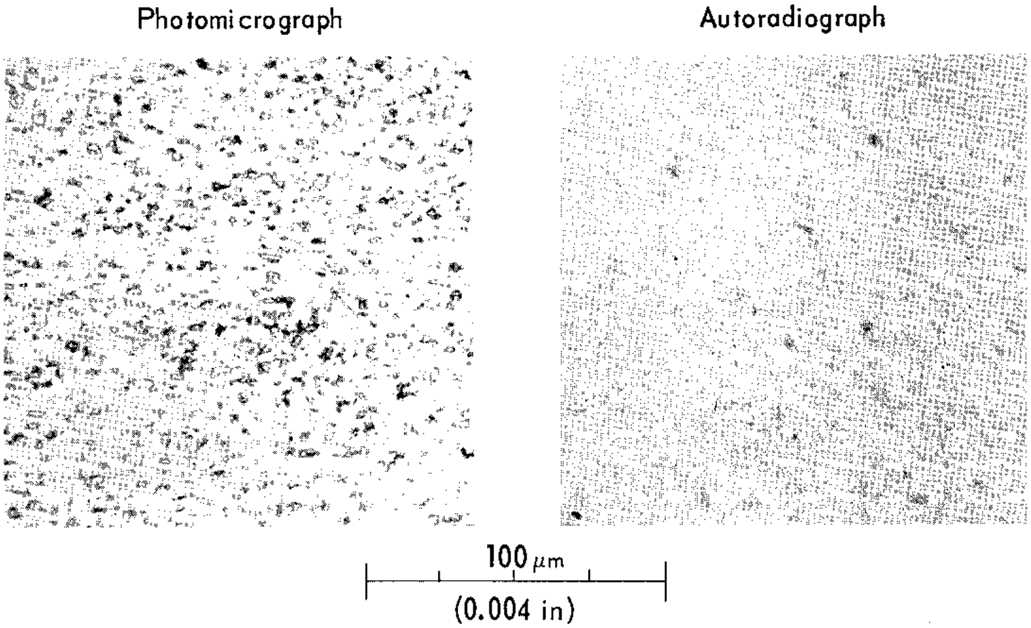


FIG. 3 NICKEL DISTRIBUTION IN 8001 ALUMINUM VS CHLORIDE ABSORPTION IN OXIDE FILM
Note that the chloride in the autoradiograph (dark dots) does not correspond to the nickel distribution in the alloy. Nickel–rich phases do not absorb chloride preferentially.

Alumina Formed on Binary Alloys

To study the effect of impurities on the absorption of chloride by aluminum, special binary alloys were prepared by vacuum melting. These alloys contained 99.9995+% aluminum plus one of the reagent-grade metals Fe, Si, or Cu, each within the concentration specifications of 1100 and 8001 alloys. After annealing, the alloys were corroded for 335 hours at 100°C in deionized water containing 1.5 ppm Cl^- with $^{36}Cl^-$ tracer. Throughout the test, pH was maintained at 5. The specimens were counted for $^{36}Cl^-$ activity, and the thicknesses of the films were measured optically (Figure 4). This figure shows that small concentrations of alloying elements can have large effects on aluminum corrosion. A summary of the absorption of chloride or the binary alloys is shown in Table IV.

TABLE IV

Chloride Absorption by Aluminum Corrosion Film on Binary Alloys

Wt % Alloying Element	Film Thickness, μm	Chloride in Film	
		μg/cm^2	ppm
0.51 Fe	2	0.13	270
0.22 Cu	9	0.054	25
0.21 Si	27	0.078	12

Iron was the most effective impurity of the three in increasing the absorption of chloride. Note that under conditions similar to those in the reactor, silicon in the tenths-weight-percent range causes very rapid corrosion. This phenomenon has been observed by others and has led to recommendation of very low[10,11] or very high[12] silicon concentrations for aluminum alloy used as cladding for nuclear fuels. These experiments indicate that an aluminum-iron alloy would be good for fuel cladding because of the thin film formed.

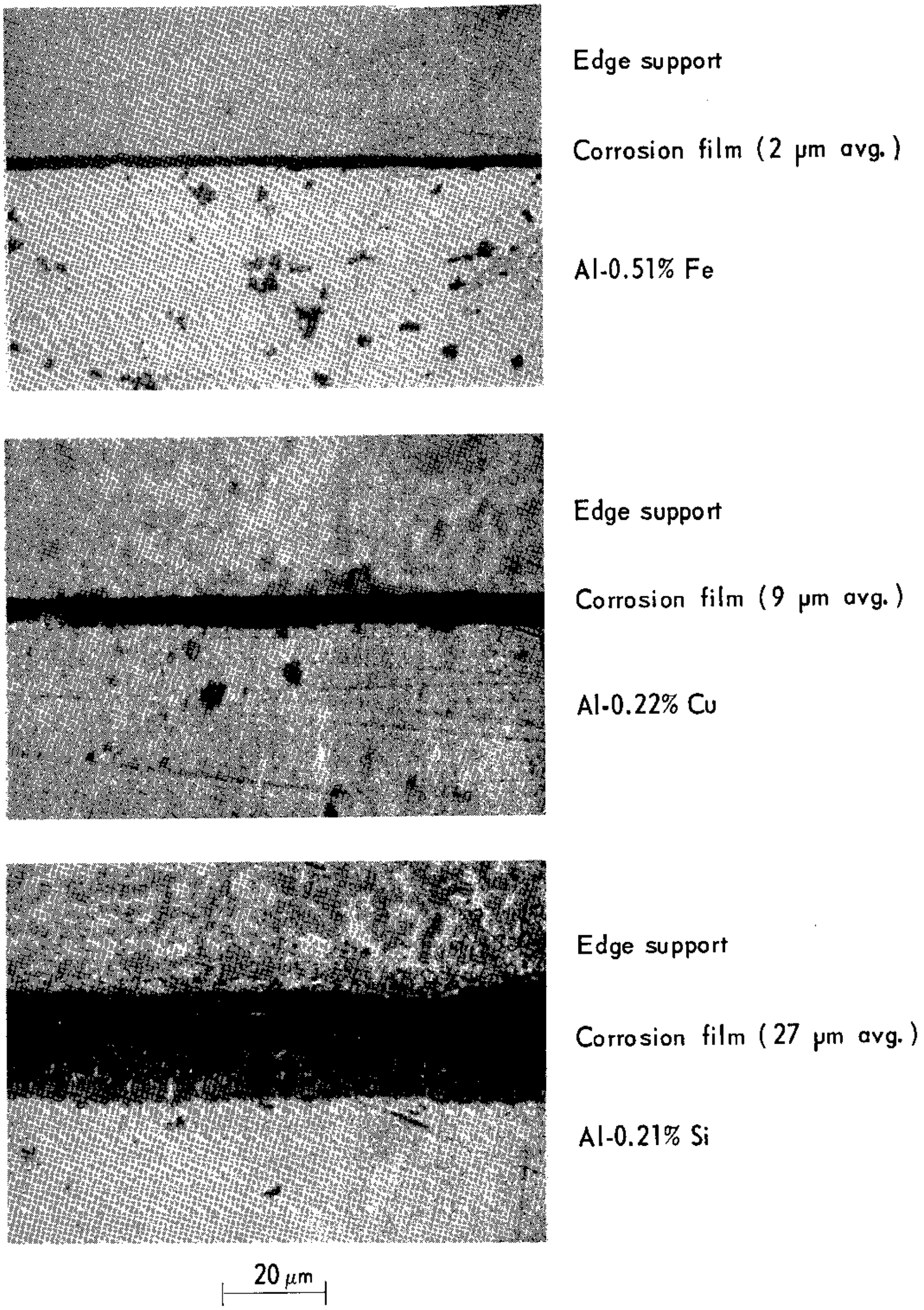


FIG. 4 CORROSION OF BINARY ALUMINUM ALLOYS
Corroded at 100°C for 335 hrs in pH 5 deionized water containing 1.5 ppm Cl^-. Note the large differences in corrosion due to small quantities of alloying agents.

DESORPTION OF CHLORIDE FROM ALUMINA

The intermittent nature of stainless steel cracking suggests that chloride release from alumina is not continuous, and may be triggered by some variable in the coolant. Therefore, the effects of H^+, CO_2, H_2O_2, NO_3^-, and $SO_4^=$, known to occur at varying concentrations in the coolant, were investigated.

A mixture of α and $\beta Al_2O_3 \cdot 3H_2O$ that contained 50 ppm of Cl^- including 4.9×10^3 counts of $^{36}Cl^-$/(min)(g) was prepared from 1100 aluminum alloy. Portions of this active alumina were added to deionized water containing one of the characteristic moderator constituents. To determine the effect of H^+, the pH was varied from 4 to 7; in all other cases, pH was held constant at 5. The temperature of the alumina suspension was held at 100°C for 200 hours, and the activity of the aqueous phase was determined periodically.

The release of chloride to the aqueous phase with changes in pH is shown in Figure 5. The smallest amount of chloride is released at pH 5. Although larger amounts are released at both higher and lower pH, pH changes in the acid direction release more chloride than equivalent changes in the less acid direction.

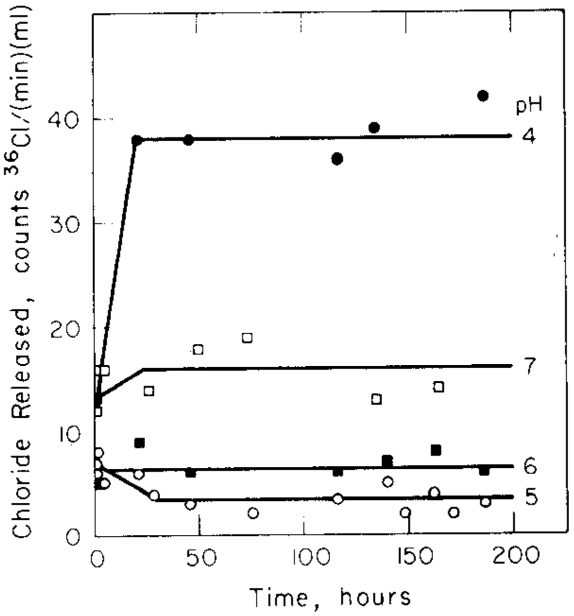


FIG. 5 EFFECT OF pH ON CHLORIDE RELEASE FROM ALUMINA

Comparison of the release of chloride to the solubility of α and $\beta Al_2O_3 \cdot 3H_2O$[4] showed a direct correlation as illustrated in Figure 6 and Table V. Figure 6 shows that the chloride release shown in Figure 5 follows the same pattern as solubility.[7] Table V gives a quantitative comparison between Figures 5 and 6.

TABLE V

Chloride Release from 1100 Aluminum Corrosion Product Compared to Alumina Solubility

pH	Relative Cl^- Released from Corrosion Product	Relative Solubility of α and $\beta Al_2O_3 \cdot 3H_2O$[4]
4	12.3	800
5	1.0	1
6	2.3	4
7	5.3	40

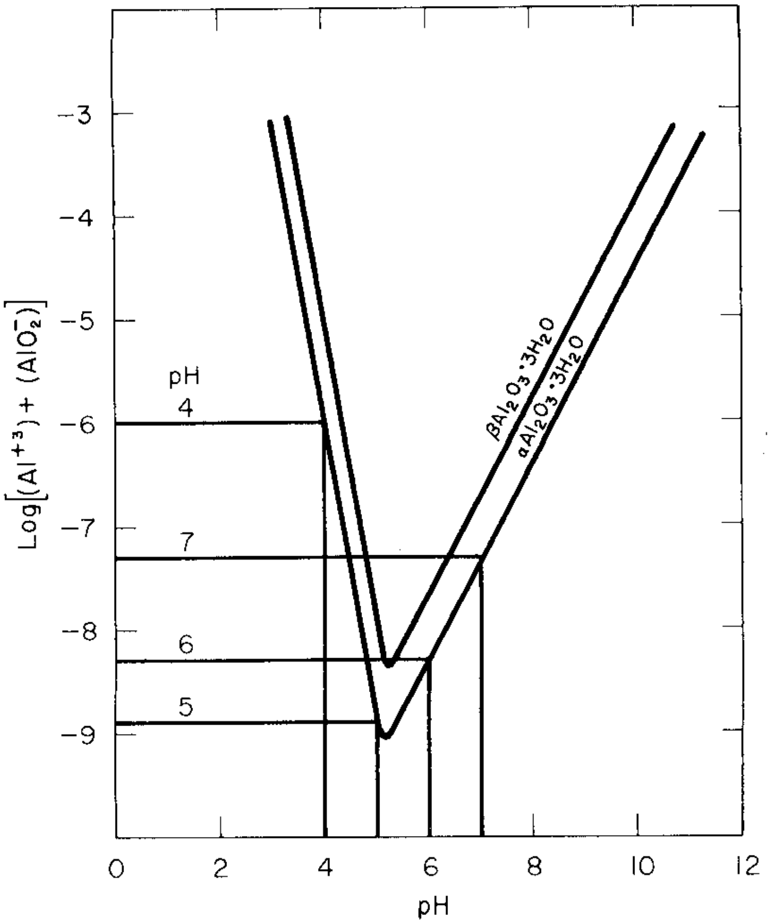


FIG. 6 SOLUBILITIES OF ALUMINA AT 25°C(2)

The pH effects on release of chloride from corrosion product are of smaller magnitude than the pH effects on the solubility of pure alumina. This distinction is attributed to the effect of iron in either preventing the release of chloride during dissolution of the alumina or decreasing the solubility of the corrosion product below that of pure alumina.

The addition of NO_3^-, CO_2, and H_2O_2 to pH 5 deionized water at 100°C containing a suspension of alumina did not affect the desorption of chloride. Table VI shows the concentrations of ions and compounds used in the experiment compared to typical moderator concentrations.

TABLE VI

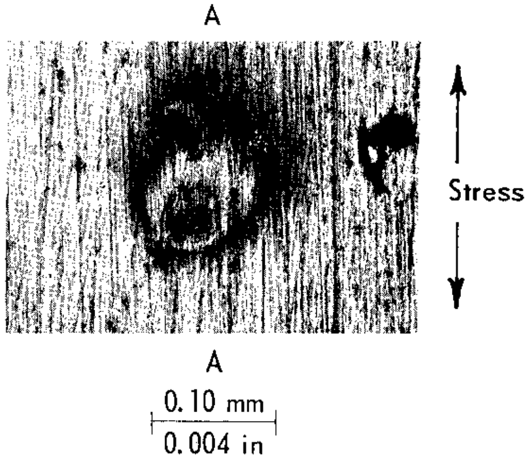
Solute Concentrations for Determining Chloride Release, ppm

Solute	Experimental Solutions	Moderator
CO_2	50-200	15
H_2O_2	5-100	2
NO_3^-	1	0.001-0.5
$SO_4^=$	0.5	0.02 -0.4

The results in the above experiment were identical to the results at pH 5 without addition of the solutes.

MECHANISM OF STAINLESS STEEL CRACKING

To test the effects of alumina containing absorbed chloride specimens of 304 stainless steel were prepared by techniques simulating those experienced by metal in the cracked portion of the reactor. The steel was sensitized, pickled with 1M HF - 4M HNO_3, dry ground, and stressed. Alumina ($\beta Al_2O_3 \cdot 3H_2O$) containing 380 ppm Cl^- was added to pH 5 deionized water to form a suspension. After 4 hours at 25°C, the aqueous phase in equilibrium with the alumina was found to contain 0.3 ±0.1 ppm Cl^-. The sample was immersed, the pH was increased to 7, and exposure was continued for up to 36 days at 90 to 95°C. Figure 7 shows one of two pits that occurred on one specimen at about 75% of the maximum stress. This



Section A-A

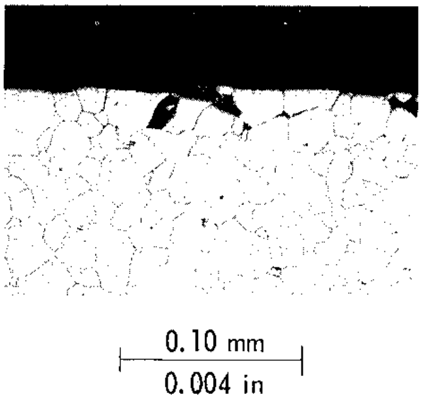


FIG. 7 PITTING OF 304 STAINLESS STEEL BY CHLORIDE-BEARING ALUMINA
Pitting due to anodic reaction. Note intergranular attack sufficient to loosen entire grains, and possible intergranular crack initiation. Grain loosening is a characteristic of the cracked areas found in the reactor system.

specimen did not crack after 240 hours exposure; a metallographic section revealed intergranular penetration to the extent that whole grains dropped from the sample, however Figure 8 shows another specimen that did crack in two locations under maximum stress. Cross sections of these cracks were typical of stress corrosion cracking.

Analysis of the solution after the 240-hour test showed 1.1 ±0.1 ppm Cl^-, equivalent to a release of 25% of the chloride that had been absorbed on the alumina. If all the chloride had been released at once, the chloride ion concentration would not have exceeded 4 ppm.

Cracked areas in the reactor system are normally coated with alumina and stained with ferric oxide (Fe_2O_3) in the cracked area. The ferric oxide shows that oxidation is taking place, and the area is therefore anodic. Oxidation of steel in an aqueous system containing oxygen occurs by Reactions 5 and 6.

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{5}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \tag{6}$$

Because Fe^{3+} is much less soluble than Fe^{2+} at pH 5, Reactions 7 and 8 occur:

$$Fe^{3+} + (3+x)H_2O \rightarrow Fe(OH)_3 \cdot xH_2O + 3H^+ \tag{7}$$

$$2Fe(OH)_3 \cdot xH_2O \rightarrow Fe_2O_3 + (3+x)H_2O \tag{8}$$

Reaction 7 produces the typically acidic reaction at an anodic location. In this localized anodic area, the pH of the solution is much lower than that of the bulk solution.

The chloride requirements for stress corrosion cracking of stainless steel in the reactor system can be expressed quantitatively. A crack can be initiated in sensitized, stressed, stainless steel at an anodic location by 5×10^{-9} g Cl^-, as shown by Overman.[13] Localized dissolution of 10 μg of alumina containing 500 ppm Cl^- could provide enough chloride at an anodic site to cause cracking, if all the chloride were adsorbed. Although it is unlikely that all the chloride would be adsorbed, the negative charge on the chloride would cause the chloride to be attracted to the positively charged anodic area. If only 50% of the chloride released from dissolving alumina were absorbed at an anodic site, a crack would require dissolution of either 10 μg of alumina containing 1000 ppm Cl^- or 20 μg of the originally assumed concentration. These assumed chloride concentrations have often been found in Savannah River reactor systems.

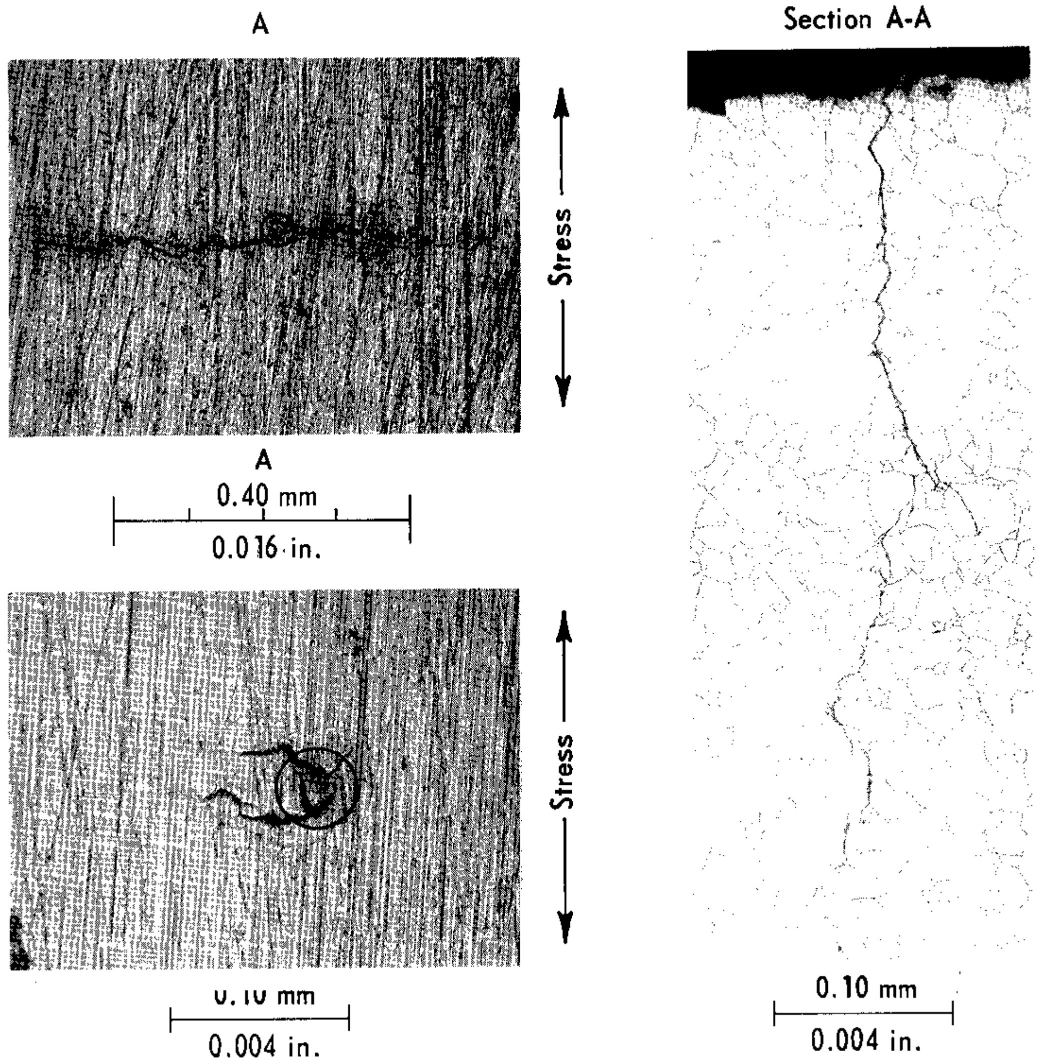


FIG. 8 CRACKING OF 304 STAINLESS STEEL BY CHLORIDE–BEARING ALUMINA
Initial anodic areas circled where chloride was released due to acid formation in pH 7 solution. Note initial intergranular and final transgranular failure, similar to cracks observed in reactor system.

MINIMIZING STAINLESS STEEL CRACKING

Deposition of chloride-bearing alumina is indicated to be a probable factor in causing occasional stress corrosion cracking of stainless steel that has been sensitized, pickled, and ground.

Based on this mechanism, sensitized metal will continue to crack at anodic sites as long as chloride-bearing alumina remains in the coolant system.

This type of cracking can be minimized by

- Maintaining the pH (pD) of the moderator-coolant between 5.0 and 5.2.
- Eliminating the use of chlorinated hydrocarbons as degreasing agents for aluminum to avoid addition of chloride to the reactor.
- Deactivating the existing anodic sites by changing the stainless steel potential, such as by installing sacrificial anodes or by adding inhibitors to the moderator.
- Removal of chloride-bearing alumina from the system.

Control of pD is already a standard procedure in normal operation of SRP reactors; practical and feasible methods for accomplishing the remaining items have not yet been established.

APPENDIX

EXPERIMENTAL PROCEDURES

Preparation of Amorphous and Crystalline Aluminas

Amorphous alumina, $Al(OH)_3 \cdot xH_2O$, was prepared by corrosion of amalgamated aluminum in water at 25°C. The specimens of aluminum were first cleaned in 1M NaOH to remove oxide, rinsed, and dipped in a 0.1M mercuric nitrate solution until the metal was coated with mercury. The specimen was then rinsed for several minutes and dipped in deionized water to corrode.

Amorphous alumina gradually transforms to crystalline alumina; the crystal form finally obtained is governed by the temperature maintained during the transformation. The α trihydrate forms by the following reactions:

$$Al(OH)_3 \cdot xH_2O \xrightarrow{>80°C} \alpha Al_2O_3 \cdot H_2O \rightarrow \beta Al_2O_3 \cdot 3H_2O \rightarrow \alpha Al_2O_3 \cdot 3H_2O$$

The β trihydrate forms as follows:

$$Al(OH)_3 \cdot xH_2O \xrightarrow{<80°C} \beta Al_2O_3 \cdot 3H_2O$$

X-ray diffraction was used to confirm transformation to the desired form.

Radioactive α and $\beta Al_2O_3 \cdot 3H_2O$ were prepared by corroding aluminum in water containing 5000 ppm Cl^- with ^{36}Cl tracer.

Solids containing ^{36}Cl were counted for beta activity by a GM counter. Solutions containing ^{36}Cl were counted by liquid scintillation techniques.

Preparation of Stainless Steel Specimens

Specimens of 304 stainless steel 3/4 x 3 x 0.060 in. thick were sensitized by heating to 625°C for 1 hour. The specimens were then pickled by swabbing with 1M HF-4M HNO_3 to remove the oxide film, rinsed, and dry ground with a 60-grit wheel. Four-point loading jigs were used to stress the specimens to a calculated 75% of yield, outer fiber stress, at room temperature.[14]

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EXTERNAL RELEASE OF TECHNICAL INFORMATION

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Author: R. S. Ondrejcin

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☒ Unclassified DP Report
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REPORT DATA SHEET

Technical Division
Savannah River Laboratory

Author(s) R. S. ONDREJCIN

Title THE CAUSE OF STRESS CORROSION CRACKING OF STAINLESS STEEL IN SRP REACTORS

Division NMD

Manuscript Approval R. S. Ondrejcin 10/30/68 Author ______ Supervisor

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Classification Approval S C [✓ U] ______ Division Head ______ TIS

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CC: L. C. Evans - J. W. Croach -
A. A. Johnson
S. A. McNeight
S. W. O'Rear - TIS File

January 28, 1970

Mr. A. F. Westerdahl, Chief
Patent Branch
Savannah River Operations Office
U. S. Atomic Energy Commission
Post Office Box A
Aiken, South Carolina 29801

Dear Mr. Westerdahl:

REQUEST FOR PATENT REVIEW

Please review for patent matter:

DP-1089 "A Mechanism for Stress Corrosion Cracking of Stainless Steel in Reactor Systems" by R. S. Ondrejcin

If any technical clarification is needed please call J. E. Beach whose document review is attached.

Please telephone your comments to the TIS Office (Ext. 3598) and notify me by signing and returning to TIS the original of this letter. A copy is provided for your file.

If you decide to pursue a patent on any development covered, I shall be happy to supply additional information required such as appropriate references and the names of persons responsible for the development.

The above item is approved
for release.

Allen F Westerdahl 2/4/70
A. F. Westerdahl Date
Chief, Patent Branch
SROO, USAEC

Very truly yours,

J. W. Croach, Director
Technical Division

By: J E Beach/swoR
J. E. Beach

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E-1177

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W File (2)

RTH Comments?
SM

February 16, 1970

R. S. Ondrejcin
Savannah River Laboratory
Building 773-A

DP-1089
A MECHANISM FOR STRESS CORROSION CRACKING OF STAINLESS STEEL IN REACTOR SYSTEMS

The preliminary copy of this report has recently been released. It concerns an investigation of the role of chloride ion in the stress-corrosion of stainless steel which is covered with deposits of alumina. The work was conducted several years ago. Stress corrosion of stainless steel was demonstrated in the laboratory under conditions in which the sole source of chloride ion was that absorbed in alumina which was applied to the surface.

In the past several years it has become evident from nuclear power plant experience that oxygen in coolant streams is uniquely responsible for the corrosion, by intergranular attack, of susceptible stainless steels. The descriptions of the plant conditions under which such corrosion was observed, supplemented by the published details of a number of laboratory investigations of these problems strongly suggest that our corrosion may also be due to the presence of oxygen (and peroxides) in our systems. Corrosion occurs in the power reactor systems at about 300°C (and in relatively shorter time periods). With this exception, the characteristics of the power reactor corrosion appear to be identical to ours:

1. Corrosion originates on the process (moderator) side.
2. The attack is exclusively intergranular (IGA). Not true!

Also, do have rust spots that are normally not observed in BWR's.

3. Only severely sensitized wrought stainless steel is involved. Neither mildly sensitized wrought material nor weld metal is attacked.

4. Intergranular attack of susceptible material occurs almost exclusively in BWR's (in which oxygen occurs at approximately 0.1 ppm). It has occurred in PWR's (which have hydrogen blankets) only in blind spots in which the atmosphere was inadvertently out of control.

5. Both BWR & PWR's have Cl^- controlled to less than 0.1 ppm.

As agreed in our telephone conversation I am enclosing photocopies of relevant literature on the role of oxygen. With this material in hand it was agreed that you would expand your report to the point that it represents current evidence in this field.

ATOMIC ENERGY DIVISION

W. B. DeLong

William B. DeLong, Director
Nuclear Materials Section

WBD/ekh

Attachment

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    DPSPU 64-11-4
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