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EFFECT OF pH AND OXYGEN ON STRESS
CORROSION CRACKING OF STAINLESS STEEL
IN REACTOR MODERATOR SERVICE

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DATA RECORD - WORKS TECHNICAL DEPARTMENT

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Introduction

Intergranular cracking of type 304 stainless steel outlet nozzles in reactor moderator service prompted a broad program of laboratory studies to determine the cause of the failures. Characteristics of the failure cracks were successfully duplicated during work reported in reference 1. It was demonstrated that sensitized and pickled type 304 stainless steel is extremely susceptible to both intergranular and transgranular chloride stress corrosion cracking in hot water of pH 4.5 to 5.0 which contains as little as 2 ppm chloride ion. Although the chloride content of moderator is only about 0.01-0.03 ppm, it was concluded that chloride concentrations sufficient to cause cracking occurred on the nozzle surfaces, either very gradually or as a result of a system change. This conclusion was substantiated later when chlorides were shown to be concentrated in a film of aluminum oxide (from fuel cladding corrosion) deposited on the moderator side of a failed nozzle.

Circumstantial evidence suggested that initiation of moderator pH (pD) control with nitric acid and oxygen caused or contributed to cracking of the nozzles. Therefore, in recent laboratory work the effects of pH and oxygen concentration on cracking of sensitized and pickled type 304 stainless steel were investigated. The effects of nitrate and sulfate ion concentrations were also investigated.

Results of these laboratory investigations are summarized in this report. Changes in the moderator system caused by pD control and the possible effects on cracking are also discussed.

Period Covered: August 1962 through August 1963.

Summary

Laboratory tests on stressed U-bend samples immersed in 90°C water with 10 ppm chloride ion concentration demonstrated that:

- ◇ The cracking tendency increased with increasing oxygen concentration. Cracking did not occur when oxygen was completely excluded.
- ◇ The cracking tendency did not vary significantly over the pH range of 7.0 to 4.0 in an air atmosphere. Mixed intergranular and transgranular cracking occurred in this range. The rate of crack propagation was 0.00014 to 0.00025 inch per hour.

- ◊ The cracking tendency changed at pH 3.5 and 3.0. Only intergranular cracking occurred, and the rate of crack propagation was faster (0.00063 inch per hour). Localized insidious intergranular corrosion produced "plugs" of damaged metal at sites of stress corrosion cracking.
- ◊ At pH 2.5 and lower, no cracking occurred.
- ◊ At pH 5.0 the cracking tendency was greater in water adjusted with sulfuric acid than that with nitric acid. In both cases, increasing the molar ratio of nitrate to chloride or sulfate to chloride decreased the cracking tendency.

Samples did not crack in solutions containing less than 1.0 ppm chloride ion.

These results indicate that, in the range of 7.0 to 4.0, moderator pD per se should not affect the cracking tendency of type 304 stainless steel in the reactor complex. However, there were changes in the moderator system caused by pD control that probably contributed to the nozzle failures. These include:

1. Deposition of chloride-bearing aluminum oxide corrosion products, providing a source of concentrated chlorides on the steel surfaces.
2. Higher concentrations of oxygen and hydrogen peroxide in the moderator after pD control than before, causing the moderator to be more corrosive to the steel.
3. Periodic contamination of the moderator with sulfate ion from cation resins, used until recently in one position of the deionizer beds, causing the moderator to be more corrosive.

Laboratory data indicate that active cracks should penetrate $\frac{1}{2}$ -inch-thick steel and become obvious as leaks within 3 to 5 months after initiation. All nozzle cracks examined to date occurred adjacent to weld repair areas where the steel was probably in a condition of extreme susceptibility. The sporadic occurrence of leaks suggests that occasional fluctuations of moderator chemistry that cause greater than normal corrosion occur, perhaps during long shutdowns or periods of peak power.

Program

Studies are being performed by SRL to determine how the cracking tendency of steel in water with very low chloride ion concentration

is affected by the deposition of aluminum oxide and by hydrogen peroxide concentration. The possibility of inhibiting cracking by the addition of nitrate to the moderator is also being investigated. Moderator analyses during reactor shutdowns (for various reasons) should be requested to determine if the concentrations of chloride and other impurities are increased for brief periods.

Discussion

Experimental Technique

Type 304 stainless steel U-bend samples, as illustrated in figure 1, were used. The steel analysis is given in table 1.

Samples were cold-formed to shape, sensitized for one hour at 1250°F, water-quenched, and then pickled in 20 vol % HNO_3 + 4 vol % HF at room temperature to remove scale and produce intergranular attack about 0.005 inch deep on all surfaces. Samples were stressed to plastic yield using type 304 stainless steel nuts and bolts (not insulated from contact), and submerged in solutions contained in wide-mouth Erlenmeyer flasks fitted with cold-finger condensers. Temperatures were maintained at 90°C by thermostatically controlled hot plates. Distilled water was used for the test solutions; chloride ion concentrations were adjusted with sodium chloride. Except where noted, pH was adjusted with nitric acid and tests were performed in a normal air atmosphere.

Effects of Oxygen

It has been reported that oxygen is necessary for chloride stress corrosion cracking and pitting of austenitic stainless steel in sodium chloride solutions^{2,3}, and that cracking time is reduced about 40% by continuously bubbling oxygen through boiling 42% magnesium chloride.⁴ Tests were performed to determine qualitatively the effect of oxygen concentration on the cracking tendency in 90°C water containing 10 ppm chloride with pH varied from 5.0 to 2.5. Quantitative analyses of the oxygen concentrations in solutions were not obtained. Oxygen was varied by the following methods.

- ◇ Complete exclusion of oxygen — obtained by bubbling argon gas through the solution and maintaining a positive argon pressure of 0.2 psig over the solution.
- ◇ Periodic exposure to air of solutions with argon bubbling and an argon blanket at atmospheric pressure. (Exposure to air occurred during brief periods when samples were removed for inspection.)

- ◊ Normal air atmosphere over the solution.
- ◊ Oxygen bubbling through the solution and an oxygen blanket at atmospheric pressure.

Test results, summarized in table 2, confirmed that oxygen is necessary for cracking and that cracking tendency increases with increasing oxygen. In the tests which produced severe cracking, the minimum times for complete penetration of the samples were not determined because continuous surveillance was not maintained. It was evident, however, that bubbling oxygen through the solutions accelerated the cracking. For example, in pH 5.0 solutions under air atmosphere cracks penetrated about 0.030 inch within 96 hours, whereas with oxygen bubbling the penetration was about 0.040 inch within 72 hours. Complete exclusion of oxygen with argon gas pressure was tested only at pH 3.0, and no cracking or corrosion stains occurred within 572 hours. Periodic exposure to air of argon-blanketed solutions over the pH range of 3.0 to 5.0 caused only slight stains and one small crack (pH 3.5). Solutions under normal air atmosphere caused cracking at each pH tested except 2.5. No damage occurred to samples in solutions at pH 2.5, even when oxygen was bubbled through. (See article on Effects of pH which follows)

Effects of pH

In order to determine the effects of pH per se on cracking tendency, a series of tests was performed in water containing 10 ppm chloride ion and in which pH was adjusted with nitric acid over the range of 7.0 to 0.0 in an air atmosphere. At each pH tested, four samples were immersed in each of five flasks containing identical solutions. The flasks were removed from the test sequentially after 24, 48, 96, 192, and 384 hours. All four samples were examined after each period. The corrosion sites were counted and all samples were flexed to reveal cracks. The worst crack was sectioned metallographically to determine maximum depth and path of cracking. Results are summarized in table 3 and in figures 2 and 3.

These tests demonstrated that, over a wide range, pH is extremely influential on stress corrosion cracking. However, the cracking tendency did not vary significantly in the pH range of 7.0 to 4.0. In this range, mixed intergranular and transgranular cracking occurred. Although the number of active corrosion sites decreased with decreasing pH, the maximum depth and propagation rate of cracks were not significantly affected, as shown in figure 2. These data indicate that the crack propagation rate is between 0.00014 and 0.00025 inch per hour. The capricious nature of chloride stress corrosion cracking was reflected by variations in the number of active sites on identical samples.

Insoluble rust-like corrosion products, probably ferric hydroxide or hydrated ferric oxide, formed in the pH range of 7.0 to 4.0. Small

randomly distributed blisters appeared on both tension and compression surfaces. These blisters were caused by the subsurface pitting corrosion described previously.¹

At pH 3.5 and 3.0, only intergranular cracking occurred; there was no evidence of transgranular cracking. The rate of propagation was about 0.00063 inch per hour, which is considerably greater than it was in the pH range of 7.0 to 4.0 as can be seen by making a comparison of figures 2 and 3.

At pH 3.5 and 3.0 insidious intergranular corrosion occurred at sites of stress corrosion cracks, producing "plugs" of damaged metal similar to those observed in 1960 near the R-Area reactor bottom shield header leak.⁵ In such areas, the grains of metal appeared to be held in place only by mechanical interlocking, as shown in figure 4. There was much less surface staining at corrosion sites, apparently because the corrosion products were more soluble in this pH range.

At pH 2.5 no cracking occurred, and the total corrosion attack was negligible. At pH 1.0 and 0.0 there was slight general intergranular corrosion beyond the initial pickling attack, but no localized penetrations occurred.

The absence of significant corrosion at pH 2.5 can be explained on the basis of Pourbaix's work.⁶ He pointed out that for heterogeneous oxidation-reduction reactions (corrosion) in dilute aqueous solutions, equilibrium is a function of electrode potential and pH. In other words, at a given pH there is an electrode potential at which equilibrium exists. Evidently, in solutions at pH 2.5, the samples developed a protective film with an electrode potential corresponding to equilibrium, and the corrosion reaction did not proceed.

Tests were performed in distilled water containing less than 1 ppm chloride ion and with pH adjusted by nitric acid over the range of pH 7.0 to 0.0. No cracking occurred in any of these solutions within times ranging from 120 to 528 hours. At pH 1.0 and 0.0 only slight general intergranular corrosion occurred beyond the initial pickling attack.

Effects of Nitrate and Sulfate Ions

It has been reported⁷ that the nitrate ion will inhibit chloride stress corrosion cracking in solutions at pH 10.5, provided that the molar ratio of nitrate to chloride ion is at least unity. Laboratory tests were performed to determine if the cracking tendency would decrease with increasing molar ratio of NO_3^- to Cl^- in 90°C water containing 10 ppm chloride ion at pH 5.0. The pH and ion ratios were adjusted with HNO_3 and NaNO_3 , respectively. Parallel tests were performed to compare the cracking tendency of samples in water with pH adjusted with H_2SO_4 and with the SO_4^{2-} to Cl^- molar ratio adjusted with Na_2SO_4 . Investigation of the effect

of the sulfate ion was prompted by moderator analyses which indicated that the sulfate and nitrate concentrations were about equal at times.

Test results, summarized in table 4, show that stress corrosion cracking occurs much more readily in water adjusted to pH 5.0 with H_2SO_4 than with HNO_3 . With a chloride ion concentration of 10 ppm, adjustment to pH 5.0 produced nitrate to chloride and sulfate to chloride molar ratios of 0.029 and 0.025, respectively. In both cases depth of cracking and number of crack sites decreased with increasing molar ratios.

Additional work is planned to evaluate the possibility of adding nitrate ions to the moderator in the range of 5 ppm or less to inhibit corrosion and cracking. Sulfate ion cannot be added as an inhibitor because it would produce undesirable sulfur radioactivity.

Possible Effects of Moderator pD Control on Cracking

The first nozzle failure was detected in R Area about four months after initiation of moderator pD control with nitric acid and oxygen, suggesting that this system change contributed to the failure. The pD was reduced from about 7.4 to 5.0 to decrease corrosion of aluminum-clad fuel elements and associated problems such as moderator turbidity.

Test results previously described in this report indicate that, in the range of 7.0 to 4.0, moderator pD per se should not affect cracking. However, increasing the oxidizing power of the moderator could contribute to cracking of susceptible steel in the system, assuming that chlorides were concentrated by some mechanism. As a result of pD control, the oxidizing power of the moderator was increased for the following reasons:

1. The amount of dissolved oxygen in the moderator has been higher after pD control was started than it was before. The oxygen concentration is always higher than the normal solubility because of radiolysis, and addition of oxygen to the blanket gas (to stabilize the nitric acid) should increase the dissolved oxygen content by decreasing the tendency for dissolved oxygen to go into the blanket gas.
2. The concentration of peroxide in the moderator increased from about 0.4 ppm to about 2 ppm. The cause of this increase is complex and not fully understood. Apparently the presence of impurities (or additives) such as NO_3^- and CO_2 cause more peroxide to be formed by radiolysis. Also, reduction of aluminum corrosion decreased the amount of deuterium evolved so there was less that could reduce the peroxide to water ($\text{D}_2 + \text{D}_2\text{O}_2 \rightarrow 2 \text{D}_2\text{O}$).

The increased oxidizing power of the moderator probably would not cause a serious corrosion or cracking problem except for the presence of chlorides. Excess oxygen and peroxide might even promote passivity. However, chlorides break the passive film, and then oxygen and peroxide stimulate anodic corrosion by acting as cathodic depolarizers.

Initiation of pD control apparently provided a mechanism by which chlorides concentrated at the steel surface, ie, absorption of chlorides by the aluminum oxide film. Analyses of the film have shown chloride concentrations up to 1000 ppm. Deposition of the film must have started after pD control was started. When the first nozzle failure occurred, the moderator side of the steel was stained a reddish-brown color. Two years later when the second failure occurred there was a grey-white film that was proven to be aluminum oxide. The reddish-brown stain was not identified, but it was quite likely the beginning of the oxide film.

Although conditions are such that cracking can occur, it is extremely significant that relatively few cracks have been detected in the five reactor systems. The three cracks examined to date were adjacent to weld repair areas where the steel was in a condition of extreme susceptibility. Probably many other such areas exist as sites for potential failures. Laboratory data on crack propagation rate indicate that active cracks should penetrate $\frac{1}{2}$ -inch-thick steel in about 3 to 5 months. The fact that the second leak in R Area occurred 2 years after the first leak suggests that occasional fluctuations occur that activate the stress corrosion cracking phenomenon. The problems of proving this and of determining how fluctuations can be eliminated or minimized remain. Additional work is required to answer such questions as:

1. How are chlorides in oxide films activated to cause cracking?
2. How is the cracking tendency affected by the redox potential of the moderator (electrode potential of the steel)?
3. To what extent does reactor power (flux intensity) affect radiolytic generation of oxygen, peroxide, or other depolarizers that stimulate corrosion and cracking?
4. Does moderator purity change significantly during shutdown, or after the reactor tank is drained to replace monitor pins or deionizer resins?

References

1. Rideout, S. P., Intergranular Cracking of Type 304 Stainless Steel - Investigation of R Reactor Outlet Nozzle Failures. E. I. du Pont de Nemours and Co., Savannah River Plant, Aiken, South Carolina. USAEC report DPSPU 62-11-26, October 1962.
2. Williams, W., and J. Eckel. J Am Soc Naval Engrs, 93-104 (February 1956).
3. Uhlig, H. H., and M. Morrill. Ind Eng Chem, 33: 875 (1941).
4. Uhlig, H. H., and J. Lincoln. J Electrochem Soc, 105: 325-332 (June 1958).
5. McKane, R. H., H. C. Minton, and J. W. Wade, Stainless Steel Failures in Savannah River Plant Reactor Areas. E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, South Carolina. USAEC report DP-539, November 1960.
6. Pourbaix, M., Thermodynamics of Dilute Aqueous Solutions. London, Edward Arnold and Co., 1949.
7. Philipps, J. H., and W. J. Singley. Corrosion, 15: 450t-454t (1959).

Table 1. Type 304 Stainless Steel Laboratory Test Material

<u>Element</u>	<u>Amount, wt %</u>
C	0.05
Cr	18.62
Ni	9.10
Mn	1.64
Si	0.47
Cu	0.24
P	0.015
S	0.018

Table 2. Effect of Oxygen on Cracking Tendency

Type 304 stainless steel (sensitized and pickled) exposed
in 90°C water containing 10 ppm chloride ion

<u>Cracking Damage After Indicated Exposure Time</u>				
<u>pH</u>	<u>Oxygen Excluded by Argon Gas Positive Pressure</u>	<u>Oxygen Content Less Than Atmospheric Argon Gas Purge No Pressure</u>	<u>Normal Air Atmosphere</u>	<u>Oxygen Saturated Solution With Oxygen Atmosphere</u>
2.5		72 hr - no damage	384 hr - no damage	72 hr - no damage
3.0	572 hr - no damage	72 hr - no damage 380 hr - no damage	48 hr - cracked, 0.036 in. penetration 96 hr - cracked, complete penetration	72 hr - cracked, complete penetration
3.5		72 hr - no damage 380 hr - slight stain, 1 small crack	48 hr - cracked, 0.045 in. penetration 96 hr - cracked, complete penetration	72 hr - cracked, complete penetration
4.0		72 hr - no damage 380 hr - stained, no cracks	48 hr - cracked, 1/3 to 1/2 penetration 96 hr - cracked, 1/2 to 2/3 penetration 384 hr - cracked, complete penetration	72 hr - cracked, 2/3 penetration
5.0		72 hr - no damage 380 hr - stained, no cracks	48 hr - cracked, 1/3 to 1/2 penetration 96 hr - cracked, 1/2 penetration 384 hr - cracked, complete penetration	72 hr - cracked, 2/3 penetration

Table 3. Effect of pH on Cracking Tendency

Type 304 stainless steel (sensitized and pickled) exposed
in 90°C water containing 10 ppm chloride ion

pH	Test Time, hr	Number of Active Corrosion Sites	Crack Path I=Intergranular T=Transgranular	Max Crack Depth, inch*	Remarks
0	24	-	I	*	General intergranular attack with no localized penetrations. Total depth after 120 hours was 0.011 inch including original pickling attack
	48	-	I	*	
	120	-	I	*	
1	24	-	I	*	General intergranular attack with no localized penetration. Total depth after 120 hours was 0.010 inch
	48	-	I	*	
	120	-	I	*	
2.5	24	-	-	*	No evidence of corrosion or cracking beyond original pickling attack of 0.005 in.
	48	-	-	*	
	96	-	-	*	
	192	-	-	*	
	384	-	-	*	
3.0	24	36	I	0.037	Localized intergranular "plug" attack at sites of cracking Complete penetration
	48	1	I	.036	
	96	10	I	.060	
	192	5	I	.060	
	384	4	I	.060	
3.5	24	12	I	.035	Localized intergranular "plug" attack at sites of cracking Complete penetration
	48	75	I	.045	
	96	19	I	.060	
	192	9	I	.060	
	384	5	I	.060	
4.0	24	8	I	.009	Some blistering due to sub-surface corrosion Complete penetration
	48	5	I & T	.033	
	96	12	I & T	.035	
	192	8	I & T	.060	
	384	2	I & T	.060	
5.0	24	36	T	.014	Some blistering due to sub-surface corrosion Complete penetration
	48	4	I & T	.016	
	96	4	I & T	.032	
	192	37	I & T	.046	
	384	15	I & T	.060	
6.0	24	20	I & T	.016	Some blistering due to sub-surface corrosion Complete penetration
	48	22	I & T	.017	
	96	9	I & T	.027	
	192	30	I & T	.052	
	384	20	I & T	.060	
7.0	24	24	T	.004	Some blistering due to sub-surface corrosion Complete penetration
	48	45	I & T	.012	
	96	39	I & T	.033	
	192	38	I & T	.060	
	384	26	I & T	0.060	

* All samples had 0.005-inch-deep intergranular pickling attack. Crack depth measurements include the depth of initial pickling damage.

Table 4. Effect of Changing Anion Molar Ratios
on Stress Corrosion Cracking

Type 304 stainless steel (sensitized and pickled) exposed in
90°C solutions at pH 5.0 containing 10 ppm chloride ion

Molar Ratio		Number of Crack Sites (Including Edge Cracks)	Max Crack Depth Away from Edges, inch
NO ₃ ⁻ to Cl ⁻	SO ₄ ⁻² to Cl ⁻		
0.029		6	0.029
.17		1	(None of these ex- tended more than 0.060 inch from edges.)
0.50		2	
2.00		1	
	0.025	31	0.054
	.11	53	.037
	0.50	11	0.028
	2.00	None	-

* Crack depth was not measured unless cracks extended more
than 0.060 inch from the edges because of the complex
effects of sheared edges.

FIGURE 1. SAMPLE USED IN STRESS CORROSION CRACKING TESTS

FIGURE 2. MAXIMUM CRACK DEPTH VERSUS TIME (pH 4, 5, 6, and 7)

FIGURE 3. MAXIMUM CRACK DEPTH VERSUS TIME (pH 2.5, 3.0, and 3.5)

FIGURE 4. INTERGRANULAR CRACKING AND "PLUG TYPE" ATTACK.

Approx 100X.

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