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INHIBITING CHLORIDE STRESS CORROSION
CRACKING IN AUSTENITIC STAINLESS STEEL

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Introduction

A practical method of inhibiting propagation of chloride stress corrosion cracking became an urgent need at the Savannah River Plant when cracking of type 304 stainless steel tubing occurred in several heat exchangers.¹ Cracks originated on the air side of the tubes at the inlet end of the exchangers where the tubes pass through a space formed by a double tube sheet. In this space, the metal temperature is approximately 90°C. Elastomer gaskets used with a carbon steel spacer ring between the tube sheets contained 8% chlorine. Some of this chlorine apparently was leached out by atmospheric condensation or tube leakage. The chloride-bearing moisture then dripped onto the tube surfaces where chloride pitting and cracking occurred.

A number of severely cracked tubes were replaced, but tubes less seriously damaged were left in service. To minimize concentration of chlorides and further cracking of tubes, a closed recirculating liquid inhibitor system was installed for flooding the space between the double tube sheets. Alkaline phosphate-sulfite solution was chosen for the inhibitor.

Concurrently, laboratory tests were begun to study chloride stress corrosion cracking of stainless steel and methods of inhibiting such cracking. Laboratory tests of the phosphate-sulfite inhibitor were included. Various phases of the program were carried out by the Savannah River Plant Engineering Assistance Section, by the Savannah River Laboratory, and by the Engineering Research Laboratory of the Du Pont Company in Wilmington, Delaware. This report summarizes results of tests performed by the Savannah River Plant Engineering Assistance Section. The tests included studies of

1. Methods of preventing chloride stress cracking and inhibiting propagation of existing cracks.
2. The propagation of existing cracks in hot air, dry sodium chloride, boiling water, and steam.
3. Methods of quantitatively measuring crack propagation during laboratory tests.
4. Possible damage to stainless steel and carbon steel by accidental concentration of inhibitors.

Period covered: October 1960 to March 1962.

Summary

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S. H. Kiser, class. officer
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An alkaline phosphate-sulfite solution prevented cracking and propagation of existing cracks in laboratory tests on U-bend samples exposed 1478 hours in water containing 100 ppm Cl⁻ at 90°C. Field

operating experience with a solution containing 1400-1600 ppm PO_4 , 50-100 ppm SO_3 , and 2000 ppm (max) SO_4 at a pH of 10.5 - 11.0 indicates that existing cracks in heat exchanger tubes are not propagating.

Other laboratory tests on type 304 stainless steel were performed to evaluate alternate inhibitors which would not require pH control or oxygen scavenging. These tests were performed in boiling 42 wt % MgCl_2 and in boiling water containing 100 ppm Cl^- (as NaCl). Test results are summarized below:

1. In boiling solutions containing 42 wt % MgCl_2 , cracking and propagation of existing cracks was prevented by:
 - a. Cathodic protection with zinc or aluminum anodes, provided electrical contact was not destroyed by corrosion.
 - b. Cathodic protection with an impressed current of 10^{-4} amp/cm².
 - c. The addition of 10 wt % sodium nitrate as a chemical inhibitor.
2. Cracks produced by one-hour exposures in boiling 42 wt % MgCl_2 did not propagate when samples were cleaned and transferred to:
 - a. Boiling distilled water for 2414 hours.
 - b. Steam at 200 psig and 300 psig for 696 hours and 264 hours, respectively.
 - c. Dry air at 170° to 200°C.
3. No cracking occurred nor did existing cracks propagate in samples buried in pure dry sodium chloride at 90°C for 310 hours.
4. In boiling water containing only 100 ppm Cl^- (as NaCl), samples cracked within 310 hours when immersed, and when suspended above the solution such that the condensate (1.0 - 1.5 ppm Cl^-) dripped onto the stressed surface. Propagation of existing cracks occurred at a slow rate under these same conditions.
5. Samples exposed in exactly the manner described in item 4 above, except that the solution contained 10 wt % sodium nitrate, showed no evidence of cracking or crack propagation after 1910 hours of exposure. The dripping condensate in this test contained 1.0 - 1.5 ppm Cl^- and 0.5 - 1.0 ppm NO_3 .
6. Type 316 stainless steel wires used to suspend samples above the uninhibited boiling water in tests described above were cracked after 929 hours. Identical wires used to suspend samples above the nitrate-inhibited water showed no evidence of cracking or corrosion after the same period.

7. In tests to determine possible corrosion damage by accidental concentration of inhibitors, stressed and unstressed samples of type 304 stainless steel were not damaged by exposure in boiling 60 wt % solutions of sodium nitrate, boiling 50 wt % sodium phosphate-sodium sulfite, and boiling 43 wt % sodium metasilicate.

Discussion

INHIBITING CRACKING OF HEAT EXCHANGER TUBES

After metallurgical investigation revealed that ruptures of type 304 SS tubes in two large heat exchangers were caused by chloride stress corrosion cracking, other similar heat exchangers were thoroughly inspected. Varying degrees of corrosion and chloride stress cracking were observed in many tubes in the space between the double tube sheets at the inlet end of the exchangers. However, no cracks were detected at the exit end or in the main body of the heat exchangers. Severely cracked tubes were replaced, but less seriously damaged tubes were left in service to avoid costly shutdowns.

In view of other experiences²⁻⁹ with chloride stress corrosion cracking under conditions which favored concentration of chloride ions, action was taken to minimize the further concentration of chlorides on these heat exchanger tube surfaces. Special low-chloride elastomer gaskets were installed with the carbon steel ring in the space between the double tube sheets, and the space itself was made part of a closed, recirculating liquid inhibitor system.

A review of the literature revealed that previous work on inhibiting chloride stress corrosion cracking was mostly limited to boiler water treatments and elimination of oxygen.⁸⁻¹¹ Based on the work of Williams,⁸ and of Phillips and Singley,¹¹ alkaline sodium phosphate water with sodium sulfite added to scavenge oxygen was chosen for startup of the inhibitor systems. The composition of this inhibitor solution was 1400 - 1600 ppm PO₄, 50 - 100 ppm SO₃, 2000 ppm (max) SO₄, and pH 10.5 to 11.0.

When the decision was made to use this inhibitor solution, laboratory tests were started to evaluate its effectiveness for arresting propagation of existing stress corrosion cracks. No crack propagation occurred in these tests (see table 4).

Operating experience with alkaline phosphate-sulfite water inhibitor has indicated that existing cracks in heat exchanger tubes are not propagating. Some tubes have actually stopped leaking, indicating that the cracks have been plugged with corrosion products or other unidentified matter in the system.

INHIBITING CRACKING IN LABORATORY TESTS

Experimental Procedure and Techniques

U-bend samples stressed to plastic yield were used in all laboratory tests. Stresses in this type of sample are complex,² and for this reason U-bend samples may be unsuitable for fundamental studies in which stress is a primary variable.¹³ However, in this work U-bend samples are appropriate because they simulate the complex situation that exists in heat exchanger tubing. Heat exchanger tubes have cold worked areas in the region of the tube sheet where stresses probably cover a broad range up to the yield stress. Also, U-bend samples are easily fabricated and are especially convenient for multiple-sample tests.

The samples were cold formed from 3-1/2 x 3/4 inch strips, sheared from a 16-gauge sheet. Type 304 stainless steel nuts and bolts (not insulated) were used to stress the samples. Except for some preliminary tests with type 304L, all samples were type 304 stainless steel. The analyses of the steels are presented in table 1, and typical samples are illustrated in figure 1. Samples used to test the ability of inhibitors to prevent propagation of existing cracks were cracked in boiling 42% MgCl₂ for 1/2 to 1 hour and then washed thoroughly in running water prior to exposure in the inhibitors. A sample typical of those used in crack propagation tests is shown in figure 3.

Tests were performed in wide-mouth Erlenmeyer flasks fitted with a Pyrex glass "cold finger" condenser to prevent loss by evaporation. Techniques for following propagation of existing cracks included, (a) measurement of electrical resistance of samples using a Corrosometer, (b) measurement of the load required to produce a constant deflection of the legs of U-bend samples, and (c) measurement of the deflection produced by a fixed load applied to the legs of the U-bend samples. Attempts to correlate crack depths measured metallographically with measurements made by methods (a) and (b) were discouraging. Method (c) proved to be satisfactory when supplemented with careful visual inspection and metallographic sections, as discussed below.

Measurements of deflection under a fixed load were obtained using a standard Rockwell Hardness Tester to which minor modifications were made, as illustrated in figure 2. A Rockwell indenter and anvil were each fitted with a 10 millimeter diameter Brinell steel ball brazed in position. Indentations for consistent seating of these modified Rockwell anvils were made on the U-bend samples (located as shown in figure 1) using a Brinell tester (10 millimeter diameter steel ball and 500 kg load). The deflection measurements were obtained as follows:

1. Seat the sample on the Rockwell matched anvils by applying the minor load.

2. Zero the dial gage.
3. Apply the major load (only the weight of the beam in this test).
4. Read deflection as the number of dial gage units traversed by the pointer during application of the major load.

The deflection readings obtained by this technique were correlated with crack depths measured metallographically on samples exposed for various times in boiling 42 wt % $MgCl_2$. The relationship between crack depth at the midpoint of the U-bend crest and time of exposure in $MgCl_2$ is shown in figure 4. Figure 5 shows crack depth versus percent change in deflection. The deflection readings became less sensitive as the number and depth of cracks increased.

An obvious weakness of this method for following crack propagation in weak aqueous solutions is that any one of the many cracks produced initially in boiling $MgCl_2$ could penetrate locally without seriously affecting the mechanical strength of the specimen. However, when localized crack propagation occurred, a rust colored corrosion product invariably accumulated along the crack at the surface of the sample. This was confirmed by metallographic sections (compare figures 7 and 9). Therefore, in tests in weak aqueous solutions deflection measurements were used only to confirm that no gross crack propagation had occurred.

Preliminary Screening Tests

At the beginning of this work, screening tests were run in several different chloride concentrations using type 304L stainless steel U-bend samples. These tests were performed to choose a solution for further detailed tests and to survey various metal nitrates as possible inhibitors. Test results are summarized in table 2. Duplicate samples were run in every test.

Boiling solutions of 42% $MgCl_2$, 45% $MnCl_2$, and 19% $FeCl_2$ + 18% $FeCl_3$ were tried. Only a few tests were run in $FeCl_2$ + $FeCl_3$ solutions because they were highly acid and corroded the samples severely. The 42% $MgCl_2$ caused severe cracking in short times with negligible corrosion of the stainless steel. Severe cracking also occurred in 45% $MnCl_2$, but longer times were required and the stainless was slightly corroded.

Various metal nitrates were added to the different chloride solutions to test their ability to prevent cracking. The nitrate ion was shown to be beneficial. Among the metal ions, silver in sufficient quantities converted all free chloride ions to insoluble $AgCl$ and thereby prevented cracking. The presence of copper always resulted in severe corrosion of the stainless steel. Except for these, there were no striking effects which could be attributed to the various metal ions, and no attempt was made to rate their relative activity.

Boiling 42% MgCl₂ was chosen for further detailed tests because of the short times required for cracking and also because of published information^{12,13,14} on the behavior of austenitic stainless steel in this solution.

Tests in Boiling 42% MgCl₂

Results of these tests are presented in table 3.

Cathodic protection was investigated, both with aluminum and zinc sacrificial anodes and with impressed current. The chemical inhibitors tested in boiling 42% MgCl₂ were sodium nitrate and sodium metasilicate. Organic chemical inhibitors were not investigated because of unsatisfactory results reported by Phillips and Singley.¹¹ Also, oxygen-scavenging inhibitors were not investigated because Uhlig and Lincoln¹⁴ reported that cracking occurs in MgCl₂ in the absence of oxygen.

Cathodic protection with zinc or aluminum washers attached to the legs of the U-bend samples prevented cracking and propagation of existing cracks, provided the sacrificial anode was not completely corroded away or the electrical contact was not broken by corrosion product buildup. Both zinc and aluminum anodes corroded severely in the boiling 42% MgCl₂.

Cathodic protection with an impressed current of 10^{-4} amp/cm² prevented cracking and crack propagation for exposure times up to 129 hours. A current density of 10^{-5} amp/cm² was insufficient protection and samples cracked within 1-1/2 hours. These results are in good agreement with Uhlig and Lincoln,¹⁴ who reported that cathodic polarization with current densities of 3×10^{-5} amp/cm² prevented cracking within the maximum time of their tests (24 hours) in boiling 42% MgCl₂.

The fact that cracking and propagation of existing cracks can be prevented by cathodic protection demonstrates the vital role played by electrochemical corrosion in chloride stress cracking. Stress alone did not cause propagation of existing cracks.

Although cathodic protection may in some field applications be a feasible method for preventing chloride stress corrosion cracking, this method is not practical for protecting large multi-tube heat exchangers.

Chemical additions of sodium metasilicate up to 1 wt % did not inhibit cracking in 42% MgCl₂. Also, U-bend samples which were dip-coated in 43% sodium metasilicate and allowed to dry prior to immersion in MgCl₂ cracked within one hour.

Although sodium nitrate additions of 1 wt % and 5 wt % did not inhibit cracking, addition of 10 wt % sodium nitrate inhibited cracking and propagation of existing cracks in tests of 584 hours duration.

Some slight pitting of the stainless steel occurred but metallographic examination revealed no cracking, as illustrated in figure 6.

The exact mechanism by which the nitrate ion inhibits cracking is not known. Obviously the addition of 10 wt % sodium nitrate represents a substantial change in the composition of the test solution and goes far beyond the normal range of compositions used for chemical inhibitors. A precipitate formed in the boiling solutions of 5 wt % and 10 wt % sodium nitrate in $MgCl_2$. This precipitate was analyzed as primarily sodium chloride. However, the availability of chloride ions for producing chloride stress corrosion cracking should not be significantly affected by precipitation of sodium chloride. Stoichiometric calculations indicate that if all sodium were precipitated as sodium chloride, the chloride ion concentration in solution would be reduced to about 86% of the original concentration. Furthermore, the addition of sodium nitrate made the boiling $MgCl_2$ solution more acid, as revealed by pH estimates made using Hydrion paper. This was substantiated by pH meter readings of samples of condensate collected from the boiling solutions. Condensate pH values were more acid than the solution, as follows:

<u>Boiling Solution</u>	<u>Solution pH*</u>	<u>Condensate pH**</u>
42 wt % $MgCl_2$	2.5	1.9
42 wt % $MgCl_2$ + 5 wt % $NaNO_3$	2.3	1.8
42 wt % $MgCl_2$ + 10 wt % $NaNO_3$	2.1	1.3

* Estimated, using Hydrion paper.

** Meter readings at room temperature.

Other investigators,¹³ have reported that increasing the acidity of boiling 42% $MgCl_2$ by HCl additions decreased time of exposure required for cracking to occur.

The inhibiting action of the nitrate ion may be due to a polarizing effect on the anodic reactions which occur during corrosion. The effect of nitrate ions on pitting corrosion of stainless steel has been discussed in detail by Greene and Fontana.¹⁶ These authors reported that, "nitrate inhibits pitting corrosion only when it is present prior to, or possibly during the early stages of, pit growth. Nitrate ion stimulates growing pits except when present in high concentrations (1.0 molar)."

Tests in Weak Aqueous Solutions

Results of these tests are presented in tables 4 and 5.

Tests were made in weak aqueous solutions (1) to determine the effectiveness of the alkaline sodium phosphate-sulfite water for inhibiting propagation of existing chloride stress corrosion cracks, and (2) to evaluate sodium nitrate and sodium metasilicate as possible alternate chemical inhibitors which would not require elimination of oxygen and/or pH control.

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Samples for crack propagation tests were initially cracked in boiling 42% $MgCl_2$ (1/2 - 1 hr), washed thoroughly, and then exposed along with uncracked samples in the test solutions. In order to simulate conditions which could occur in an inhibitor system vapor phase, samples were also suspended above the hot solutions such that the condensate dripped onto the tensile-stressed surface of the U-bends. The inhibitors were evaluated in chloride-free water and in water containing 100 ppm chloride ion (as NaCl).

Cracking and crack propagation occurred in both immersed and suspended samples in uninhibited water containing 100 ppm chloride ion. The pH of the water was 5.0 - 5.5. Also, stainless steel wires (types 316 and 304) used to suspend the samples in the vapor phase of this solution were cracked within 929 hours. These results were surprising because of the low chloride level and low temperature. Also, the stresses in the wires were only residual stresses plus the weight of the sample.

Cracking and/or propagation of cracks under these conditions was always evidenced by a visible red-rust corrosion product buildup. Figure 7 illustrates this on a sample which was immersed in uninhibited water (100 ppm Cl^-) after being initially cracked in $MgCl_2$. The sites of active corrosion cracking are clear. An initially uncracked sample, which cracked at an area of localized corrosion while suspended in the vapor phase, is illustrated in figure 8. This sample was never immersed in the liquid but was wetted by condensate which contained only 1.0 - 1.5 ppm Cl^- . In this case there was evidence of microscopic corrosion pits from which cracks initiated (see metallographic section in figure 8). The abundance of oxygen in the vapor phase probably stimulated corrosion pitting^{5,17}; chloride ions could then concentrate in the pits to a degree sufficient to cause cracking.

Other initially uncracked samples developed rust spots along the sheared edges, and metallographic sectioning confirmed cracking had occurred. This confirms reports of other investigators that cracks initiate most readily in cold-worked metal. Scharfstein and Brindley¹⁵ reported that chloride stress corrosion cracking occurs in low-chloride water below the boiling temperature. In their tests, the pH was 6 - 8, but the beneficial effects of the phosphate ion in more alkaline solutions of pH 10 - 11 were discussed.

In the present work, tests of the alkaline sodium phosphate-sulfite water inhibitor were run both with and without a nitrogen blanket to protect against loss of the sulfite. No propagation of existing cracks occurred in any of these tests (table 4), indicating that at this low-chloride level, the alkaline phosphate solution without oxygen scavenging was sufficient to inhibit crack propagation.

The addition of 10 wt % sodium nitrate to water containing 100 ppm Cl^- prevented cracking and crack propagation in both immersed and suspended samples (table 5). The pH of the 100 ppm Cl^- water changed, but only from 5.6 to 6.0 when nitrate was added. The condensate from these inhibited solutions contained 1.0 - 1.5 ppm Cl^- and

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0.5 - 1.0 ppm NO_3^- . The fact that samples and wires in the vapor phase did not crack in these tests indicates that a considerably lower concentration of nitrate ion would inhibit cracking in weak aqueous solutions. This was not investigated in the present work. However, Phillips and Singley¹¹ reported that cracking did not occur in type 347 stainless steel in tilting autoclave tests at 500°F when the mole ratio of nitrate to chloride was at least unity and pH was higher than 10.5.

Tests using sodium metasilicate were limited to concentrations of 100 ppm and 1500 ppm. Evidence of localized corrosion attack (spots of red rust) appeared on all samples except those immersed in water containing 1500 ppm of the inhibitor (table 5).

Propagation of Existing Cracks

While tests were being conducted in concentrated chloride solutions and in weak aqueous solutions, other tests were performed simultaneously on samples initially cracked in MgCl_2 to determine the tendency for existing chloride stress corrosion cracks to propagate in the following environments. Uncracked control samples were similarly tested.

Hot dry air (170° - 200°C)
Pure dry sodium chloride (90°C)
Boiling distilled water (100°C)
Steam [200 psig (197°C) - 300 psig (216°C)]

No cracking or crack propagation occurred in hot dry air or dry sodium chloride, although in both environments existing cracks were oxidized (see table 6).

Exposures up to 2414 hours in boiling distilled water caused only slight staining of the surface around existing cracks, as illustrated in figure 9. Very slight increases of deflection under fixed load were observed, but metallographic examination of sections through several samples revealed no evidence of crack propagation. Some yawning and oxidation of existing cracks was noted.

There was no evidence of crack propagation in samples exposed 696 hours in steam at 200 psig or at 300 psig for 264 hours. The deflection measurements actually were slightly less after exposure in steam. The existing cracks were filled with oxide, which would prevent them from serving as crevices in which chloride ions could concentrate. No new cracks were detected, probably because the steam contained less than 1 ppm Cl^- , the temperature was low, and alternate wetting-drying did not occur.

These test results demonstrate that continued electrochemical corrosion is required for propagation of existing cracks. Electrochemical corrosion did not occur in the absence of water, and the corrosion in distilled water and steam was insufficient to propagate cracks.

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Corrosion Damage by Inhibitors

Tests were performed to determine the degree of possible corrosion damage to type 304 stainless steel and type 1020 carbon steel, if the chemical inhibitors under investigation were accidentally concentrated within the aqueous inhibitor system. Results of these tests are presented in tables 7 and 8.

Stressed and unstressed type 304 stainless samples were exposed for 1066 hours in boiling solutions of concentrated sodium nitrate and sodium phosphate-sodium sulfite (table 7). Samples exposed in a concentrated solution of sodium metasilicate were discontinued after 40 hours when the flask dissolved. None of the samples tested showed any corrosion damage. However, the samples exposed in sodium phosphate-sodium sulfite were covered with a thin, gray-white film which was very adherent though porous. This film could not be removed by brushing in soap and water, but was successfully removed at the end of the test by alternately dipping the samples in a pickling solution of 10 ml H_2SO_4 (sp gr 1.84), 3g NaCl, and 90 ml of H_2O at $160^\circ - 180^\circ F$ and brushing in water. The surface of the stainless steel showed little evidence of corrosive attack and the corrosion rate of the samples ranged from 0.00004 to 0.00005 inch per month.

Stressed type 304 stainless samples with carbon steel bolt couples, and unstressed carbon steel samples, were exposed for 638 hours in a boiling solution of 10 wt % $NaNO_3$ (table 8). The stainless samples were stained where they made contact with the carbon steel bolt, but they showed little evidence of corrosive attack (see figure 10). However, the carbon steel bolts were stained and slightly corroded as evidenced by corrosion rates varying from 0.00031 to 0.00040 inch per month. The unstressed carbon steel samples were also stained and slightly corroded, with corrosion rates varying from 0.00015 to 0.00017 inch per month.

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Table 1. Chemical Compositions* of Stainless Steels Used in Laboratory Tests

Element,* wt %	AISI Type 304	AISI Type 304L
	(J & L Heat No. 57191)	(Armco Heat No. 67381)
C	0.052	0.040
N	0.006	0.003
Cr	18.62	17.85
Ni	9.10	9.49
Mn	1.64	1.28
Si	0.47	0.50
Cu	0.24	0.16
P	0.015	0.011
S	0.018	0.015

* Check-analyses on mill-finished sheets.
Ladle-analyses were not readily available.

Table 2. Preliminary Screening Tests on Type 304L U-Bend Samples

Solution	Time, hr	Results	
		Stress Cracking	General Corrosion
42% MgCl ₂	61	Very severely cracked	Slightly stained
42% MgCl ₂ + 5% Cu(NO ₃) ₂	61	Cracked but not broken	Slightly corroded
42% MgCl ₂ + 5% Pb(NO ₃) ₂	61	Cracked but not broken	Slightly stained
42% MgCl ₂ + 5% Zn(NO ₃) ₂	61	Severely cracked	Slightly stained
45% MnCl ₂	61	Severely cracked	Stained, slightly corroded
45% MnCl ₂ + 5% Cu(NO ₃) ₂	61	Cracked, not broken	Severely corroded
45% MnCl ₂ + 5% Pb(NO ₃) ₂	61	No cracks	Stained, slightly corroded
45% MnCl ₂ + 5% Zn(NO ₃) ₂	61	No cracks	Stained, slightly corroded
19% FeCl ₂ + 18% FeCl ₃	22	Severely cracked	Severely corroded
19% FeCl ₂ + 18% FeCl ₃ + 5% Cu(NO ₃) ₂	22	-	Samples dissolved
19% FeCl ₂ + 18% FeCl ₃ + 5% Pb(NO ₃) ₂	22	-	Samples dissolved
19% FeCl ₂ + 18% FeCl ₃ + 5% Zn(NO ₃) ₂	22	-	Samples dissolved
19% FeCl ₂ + 18% FeCl ₃ + 5% Sn(NO ₃) ₂	22	No cracks	Severely corroded
45% MnCl ₂ + 5% CuCl ₂	22	Severely cracked	Slightly corroded
42% MgCl ₂ + 5% NaNO ₃	72	Many cracks, none penetrated	Slightly corroded
45% MnCl ₂ + 4.7% Mn(NO ₃) ₂	72	No cracks	Slightly stained
45% MnCl ₂ + 3.6% ZnCl ₂	65	Severely cracked	Slightly stained
45% MnCl ₂ + 5% CuCO ₃	42	Severely cracked	Severely corroded
45% MnCl ₂ + 5% NaNO ₃	49	No cracks	Slightly stained
2.5% MgCl ₂ + 8.2% AgNO ₃	72	No cracks	Slightly corroded
2.5% MgCl ₂ + 8.2% AgNO ₃	1072	No cracks	Slightly corroded
2.5% MgCl ₂	952	No cracks	Slightly corroded

Table 3. Inhibiting Chloride Stress Corrosion
Cracking in Boiling 42% MgCl₂

	No. and Type of Samples	Time, hr	Avg Change in Deflect- ion, %	Remarks
Cathodic Protection				
Zinc Washer, g				
2.3	1 uncracked	20	>100	Samples cracked after zinc corroded away.
2.3	1 cracked	20	>100	Samples cracked after zinc corroded away.
4.9	1 uncracked	938	+8.2	No evidence of cracking. Zinc was heavily corroded.
5.8	1 cracked	938	-9.2	No evidence of crack propagation. Zinc was heavily corroded.
13.3	1 uncracked	936	+5.7	No evidence of cracking. Gray film on sample.
18.3	1 cracked	936	0	No evidence of crack propagation. Gray film on sample.
Type 25 Al Washer, g				
0.6	1 uncracked	547	>100	Sample cracked after aluminum corroded away.
0.6	1 cracked	547	>100	Sample cracked after aluminum corroded away.
1.4	1 uncracked	817	-2.5	No evidence of cracking. White film on sample.
1.3	1 cracked	817	+3.2	No evidence of crack propagation. White film on sample.
Type B605 Al (Al + 5% Zn) Washer, g				
1.2	2 uncracked	338	>100	Samples cracked after washer corroded away.
0.9	2 cracked	235	>100	Samples cracked after washer corroded away.
Impressed Current				
10 ⁻⁵ amp/cm ²	2 uncracked	1.5	+36.2	Samples cracked.
10 ⁻⁴ amp/cm ²	2 uncracked	129	+1.5	No evidence of cracking. Surface film.
Chemical Inhibitor				
Na₂SiO₃				
0.5% (soluble)	2 uncracked	1.5	>100	Samples cracked.
0.5% (soluble)	2 cracked	1.5	>100	Cracks propagated.
1.0% (not all soluble)	2 uncracked	1.5	>100	Samples cracked.
1.0% (not all soluble)	2 cracked	1.5	>100	Cracks propagated.
4% (dip coat)	2 uncracked	16	>100	Coating blistered within 15 min, sample cracked.
NaNO₂				
1% (soluble)	2 uncracked	1.5	>100	Samples cracked.
1% (soluble)	2 cracked	1.5	>100	Cracks propagated.
5% (NaCl Precipitate)	2 uncracked	15.0	>100	Samples cracked.
5% (NaCl Precipitate)	2 cracked	15.0	>100	Cracks propagated.
10% (NaCl Precipitate)	2 uncracked	584	+6.9	No cracking. Slight corrosion pitting (see figure 6).
10% (NaCl Precipitate)	2 cracked	584	-6.9	No crack propagation. Slight pitting.

Table 4. Inhibiting Propagation of Existing Cracks
With Alkaline Phosphate-Sulfite Water*

Test No.**	Sample Location	Atmosphere	Cl-ppm	Temp, °C	Exposure Time, hr	Avg Change in Deflection, %
1	Immersed in Liquid	Nitrogen Gas Blanket	0	90	1478	+1.7
2	Immersed in Liquid	Nitrogen Gas Blanket	100	90	1672	-0.4
3a	Suspended in Vapors (Condensate Dripping)	Air & Vapors	100	60-90	954	2.6
3b	Immersed in Liquid	Air & Vapors	100	100 (Boiling)	954	1.2

* PO₄ = 1400 - 1600 ppm
SO₃ = 50 - 100 ppm
SO₄ = 2000 ppm (max)
pH = 10.5 - 11.0

** 4 cracked samples in each test. There was
no crack propagation in any of the tests.

Table 5. Inhibiting Stress Corrosion Cracking in Boiling Water Containing 100 ppm Chloride (as NaCl)

Inhibitor	Conc	Number and Type of Samples	Time, hr	Avg Change in Deflection, %		Remarks
None		4 (uncracked) immersed	310 (1) 1910 (3)	+6.1 +4.9	Metallography on 2 samples revealed cracking under rust-colored corrosion stains which were present on all samples, mostly along sheared edges.	
None		4 (uncracked) suspended in vapors (condensate dripping)	310 (1) 1910 (3)	0 +5.0		
None		4 (cracked) immersed	310 (1) 1910 (3)	-8.2 +7.4		
None		4 (cracked) suspended in vapors (condensate dripping)	310 (1) 1910 (3)	+3.8 +6.6		
NaNO ₃	10 wt %	4 (uncracked) immersed	256 (1) 1910 (3)	+3.6 -2.6	No corrosion or cracking.	
NaNO ₃	10 wt %	4 (uncracked) suspended in vapors (condensate dripping)	256 (1) 1910 (3)	-2.0 -1.4		
NaNO ₃	10 wt %	4 (cracked) immersed	256 (1) 1910 (3)	+1.7 +2.6		
NaNO ₃	10 wt %	4 (cracked) suspended in vapors (condensate dripping)	256 (1) 1910 (3)	+5.3 +0.6		
Na ₂ SiO ₃	100 ppm	1 (uncracked) immersed	2294	+13.6	Corrosion spots along sheared edges, indicated cracking.	
Na ₂ SiO ₃	100 ppm	1 (uncracked) suspended in vapors (condensate dripping)	2294	+9.3		
Na ₂ SiO ₃	100 ppm	1 (cracked) immersed	2294	+6.6	Crack propagation. Corrosion spots along sheared edges, indicated cracking.	
Na ₂ SiO ₃	100 ppm	1 (cracked) suspended in vapors (condensate dripping)	2294	+7.2		
Na ₂ SiO ₃	1500 ppm	1 (uncracked) immersed	2294	+4.6	No evidence of corrosion.	
Na ₂ SiO ₃	1500 ppm	1 (uncracked) suspended in vapors (condensate dripping)	2294	+11.1	Corrosion spots along sheared edges.	
Na ₂ SiO ₃	1500 ppm	1 (cracked) immersed	2294	+5.7	Light corrosion stains around cracks.	
Na ₂ SiO ₃	1500 ppm	1 (cracked) suspended in vapor (condensate dripping)	2294	+7.0	Corrosion product buildup in some cracks.	

Table 6. Propagation of Existing Cracks

Environment	No. and Type of Samples	Temp, °C	Time, hr	Change in Deflection, %		Remarks
				Range	Avg	
Dry Air	3 (cracked)	170 - 200	384	-3.6 to +0.8	-1.7	Oxidation of surface and in cracks. No propagation.
Dry Air	3 (uncracked)	170 - 200	384			Oxidation of Surface.
Pure Dry NaCl	2 (cracked)	90 - 95	310	-4.1 to -2.7	-3.4	Oxidation in cracks. No propagation.
Pure Dry NaCl	2 (uncracked)	90 - 95	310			No oxidation.
Boiling Distilled Water	12 (cracked)	100	2414	-2.7 to +11.5	+8.0	Very light stain around some cracks. No propagation (see figure 9).
Boiling Distilled Water	12 (uncracked)	100	2414	0 to +12.5	+4.5	No cracks or corrosion.
Steam at 300 psig	6 (cracked)	216	144	-17.3 to +17.1	-2.0	Slate gray oxide on surface and in cracks. No propagation.
Steam at 300 psig	6 (cracked)	216	264	-28.4 to -4.6	-13.3	Same as above.
Steam at 200 psig	6 (cracked)	197	696	-17.5 to -4.5	-9.8	Same as above.
Steam at 200 psig	6 (cracked)	197	336	0 to +1.9	+0.9	Slate-gray oxide on surface.

Table 7. Corrosion Damage to Stainless Steel by Concentrated Inhibitors

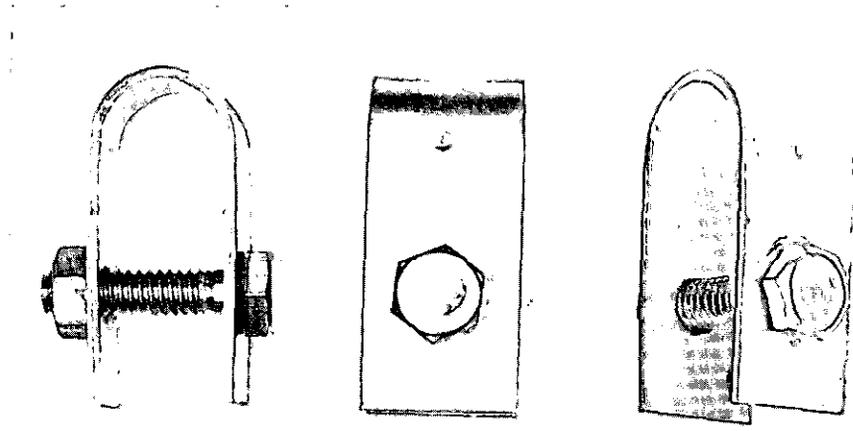
Sample	Description	Solution	Conc, wt %	Temp, °C	Time, hr	Weight Change, g	Corrosion Rate, in./mo	Remarks
B78	SS U-Bend	NaNO ₃	25	104	1066	+0.0013	-	No damage or corrosion
B79	SS U-Bend	NaNO ₃	25	104	1066	-0.0001	-	
B80	SS U-Bend	NaNO ₃	60	112	1066	+0.0006	-	
B81	SS U-Bend	NaNO ₃	60	112	1066	+0.0003	-	
B82	SS U-Bend	PO ₄ -SO ₂	50*	102	1066	-0.0412	0.00005	
B83	SS U-Bend	PO ₄ -SO ₂	50*	102	1066	-0.0436	0.00005	
B84	SS U-Bend	Na ₂ SiO ₃	43	118	40**	+0.0002	-	No damage or corrosion.
B85	SS U-Bend	Na ₂ SiO ₃	43	118	40**	+0.0014	-	
B88	SS Flat Plate	NaNO ₃	25	104	1066	-0.0002	-	No damage or corrosion.
B89	SS Flat Plate	NaNO ₃	25	104	1066	-0.0003	-	
B90	SS Flat Plate	NaNO ₃	60	112	1066	+0.0001	-	
B91	SS Flat Plate	NaNO ₃	60	112	1066	+0.0002	-	
B92	SS Flat Plate	PO ₄ -SO ₂	50*	102	1066	-0.0408	0.00005	
B93	SS Flat Plate	PO ₄ -SO ₂	50*	102	1066	-0.0374	0.00004	
B94	SS Flat Plate	Na ₂ SiO ₃	43	118	40**	+0.0008	-	No damage or corrosion.
B95	SS Flat Plate	Na ₂ SiO ₃	43	118	40**	+0.0007	-	

* 46.7% Na₂HPO₄ - 3.3% Na₂SO₃.

** Flask dissolved after 40 hours.

Table 8. Corrosion Damage to Carbon Steel and Stainless Steel-Carbon Steel Couples by 10 wt % NaNO₃ in Water

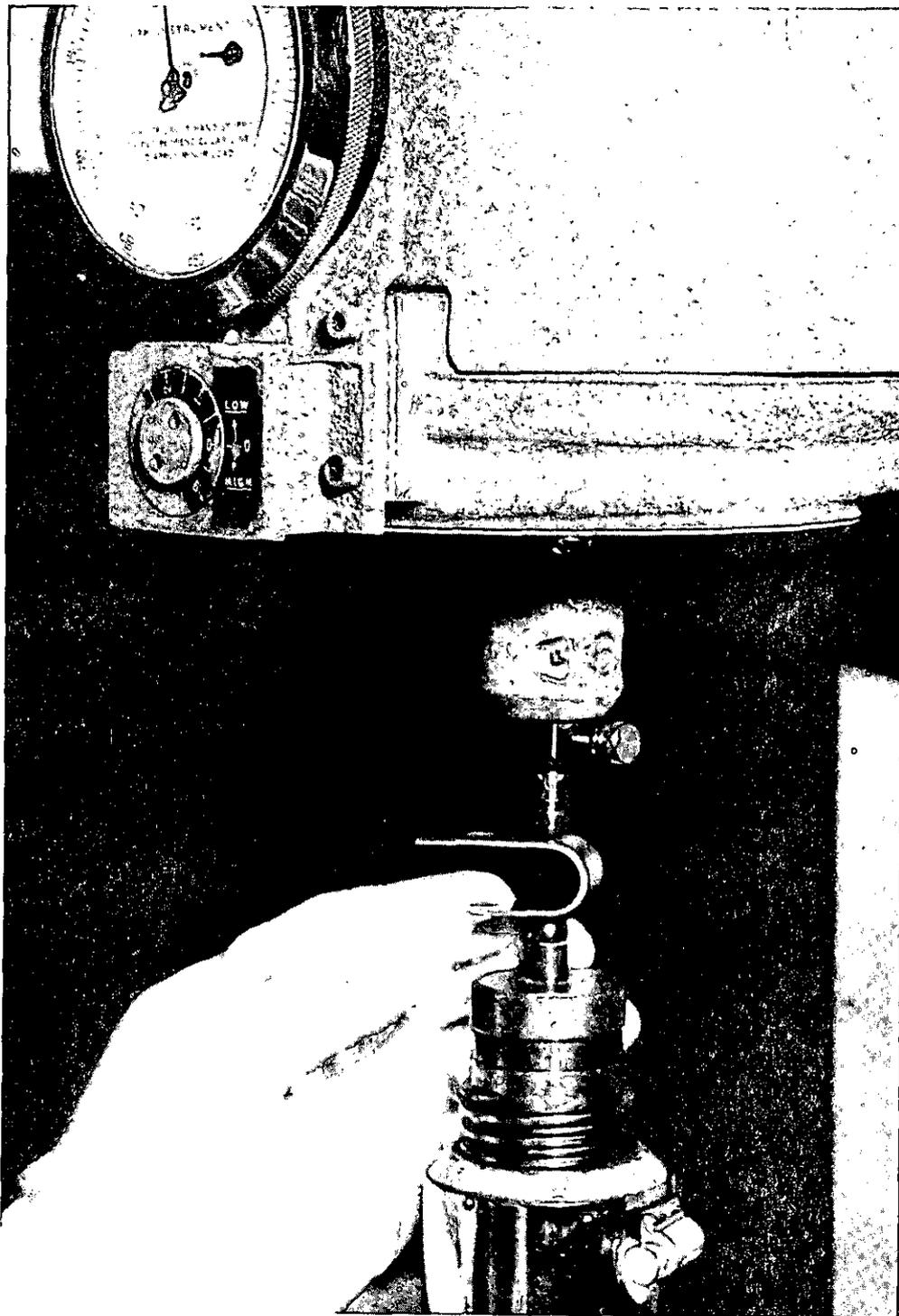
Sample	Description	Solution Temp, °C	Time, hr	Weight Loss, g	Corrosion Rate, in./mo	Remarks
C78	SS U-Bend	100	638	0.0057	0.00001	No visible corrosion - stained where in contact with bolt. Stained and slightly corroded.
	CS Bolt			0.0685	0.00031	
C79	SS U-Bend	100	638	0.0058	0.00001	No visible corrosion - stained where in contact with bolt. Stained and slightly corroded.
	CS Bolt			0.0891	0.00040	
C80	SS U-Bend	100	638	0.0048	0.00001	No visible corrosion - stained where in contact with bolt. Stained and slightly corroded.
	CS Bolt			0.0763	0.00034	
C51	CS Flat Plate	100	638	0.0549	0.00016	Stained and slightly corroded.
C52	CS Flat Plate	100	638	0.0501	0.00015	Stained and slightly corroded.
C53	CS Flat Plate	100	638	0.0569	0.00017	Stained and slightly corroded.



Approx 1X

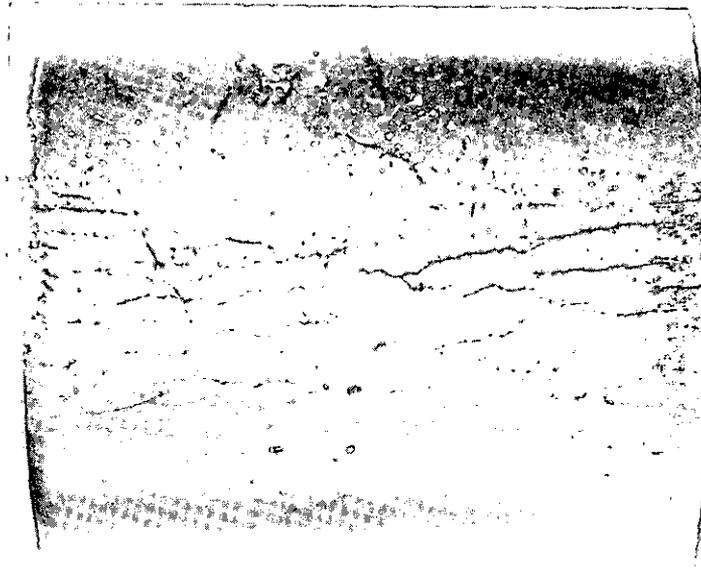
Neg EA-5503-A

FIGURE 1. TYPE 304 STAINLESS STEEL U-BEND SAMPLES USED IN CHLORIDE STRESS CRACKING TESTS. Note positioning indentations for seating deflection tester anvils.



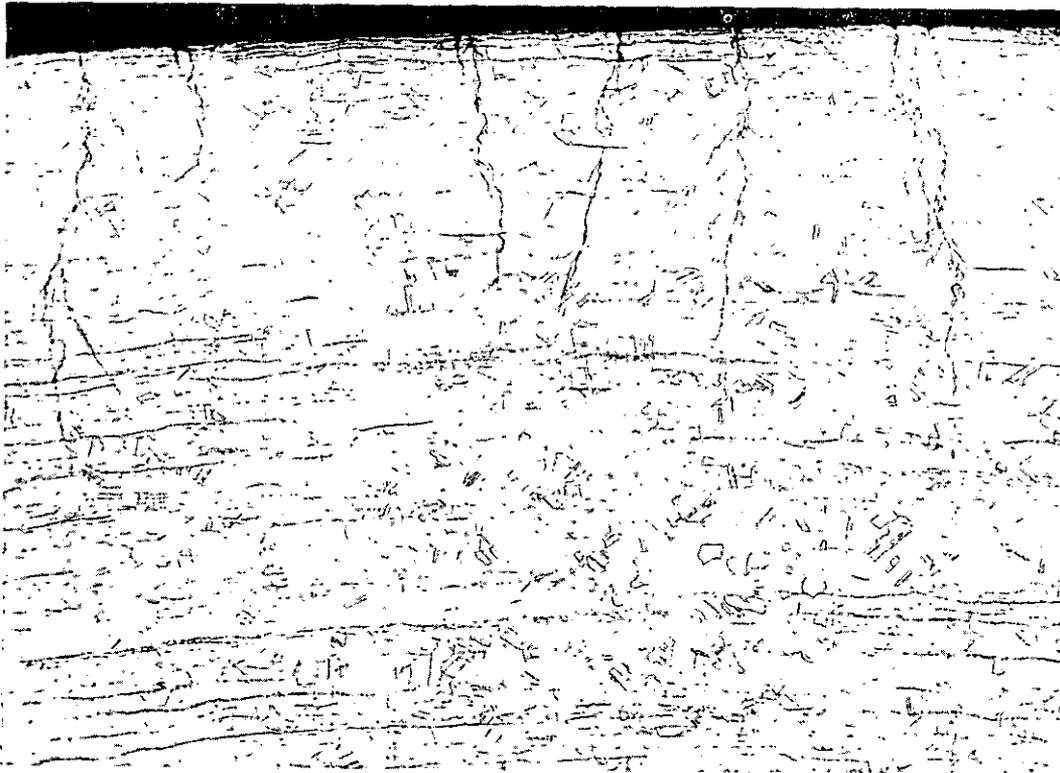
Neg EA-6956-A

FIGURE 2. METHOD OF MEASURING U-BEND SAMPLE DEFLECTION. Note the anvil and indenter of the hardness tester have been replaced by 10 mm diameter steel-ball anvils for positioning the sample. Only the weight of the beam was used for the major load.



Approx 5X

Neg EA-5505-A



Approx 100X

Neg EA-6958-A

FIGURE 3. TYPICAL CRACKED SAMPLE USED IN CRACK PROPAGATION TEST. This degree of cracking was produced by 1 hour exposure in boiling 42% $MgCl_2$. Section was through the middle of the sample.

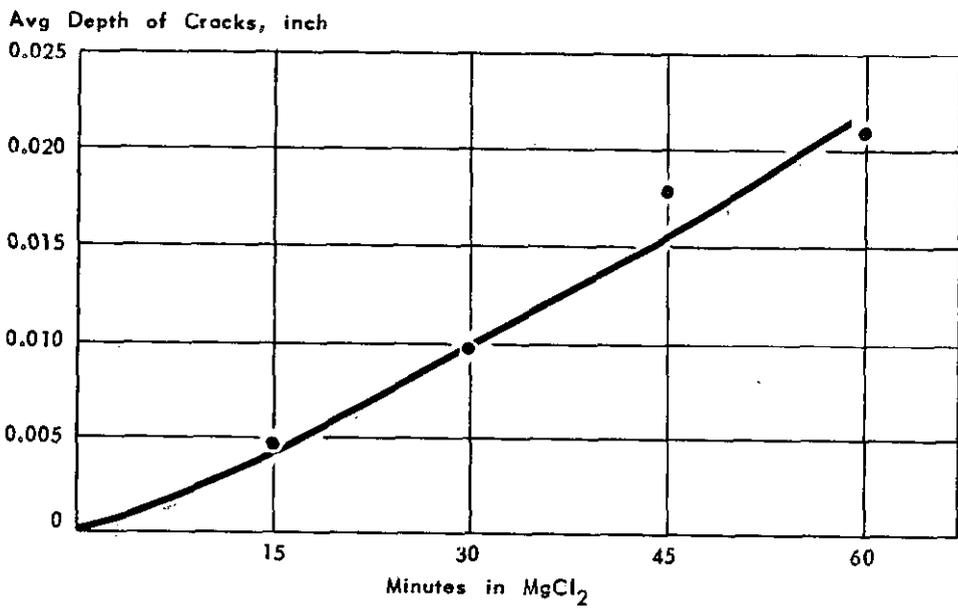


FIGURE 4. CRACKING OF TYPE 304 STAINLESS STEEL IN BOILING 42% MgCl₂

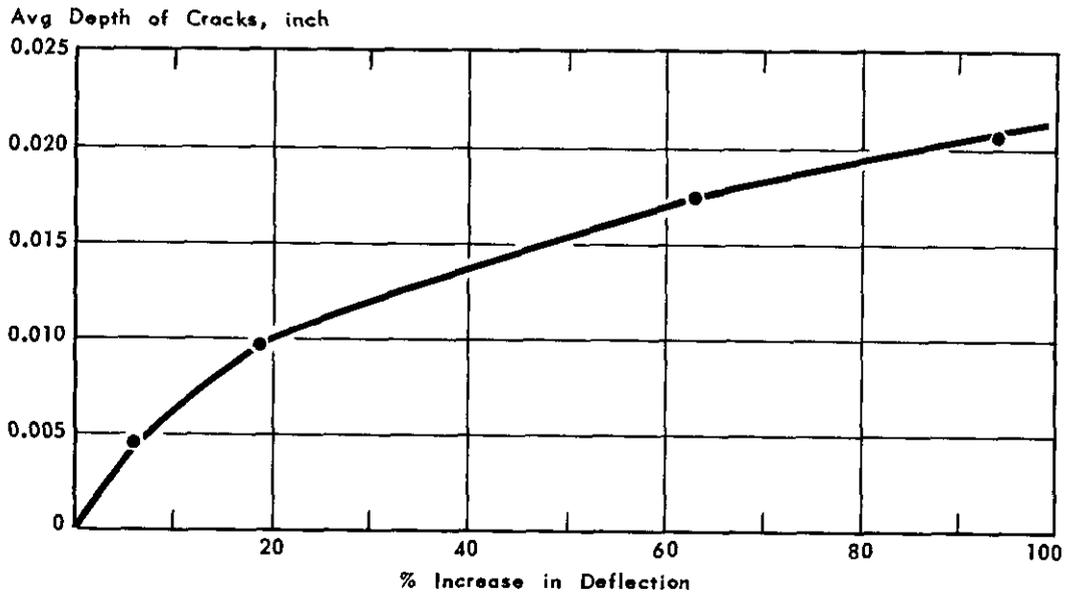


FIGURE 5. RELATIONSHIP BETWEEN CRACK DEPTH AND FIXED-LOAD DEFLECTION

UNCLASSIFIED



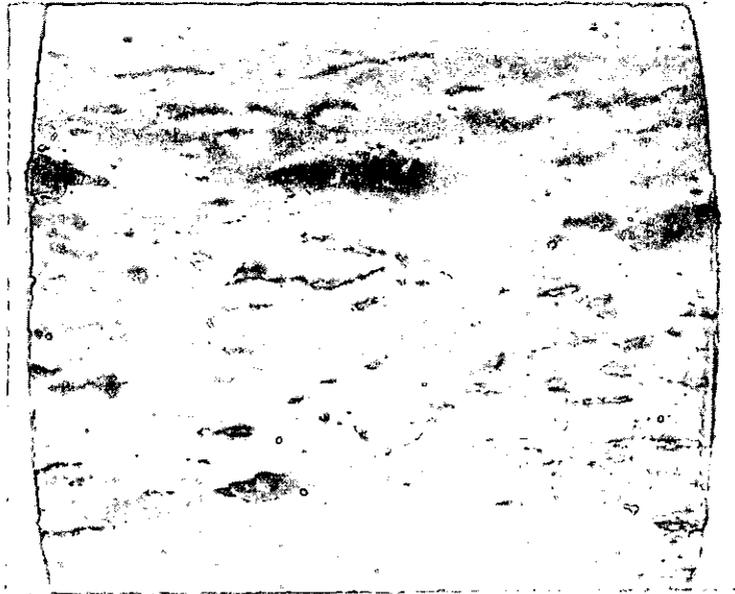
Approx 250X

Electrolytic Oxalic Acid Etch

Neg EA-5501-A

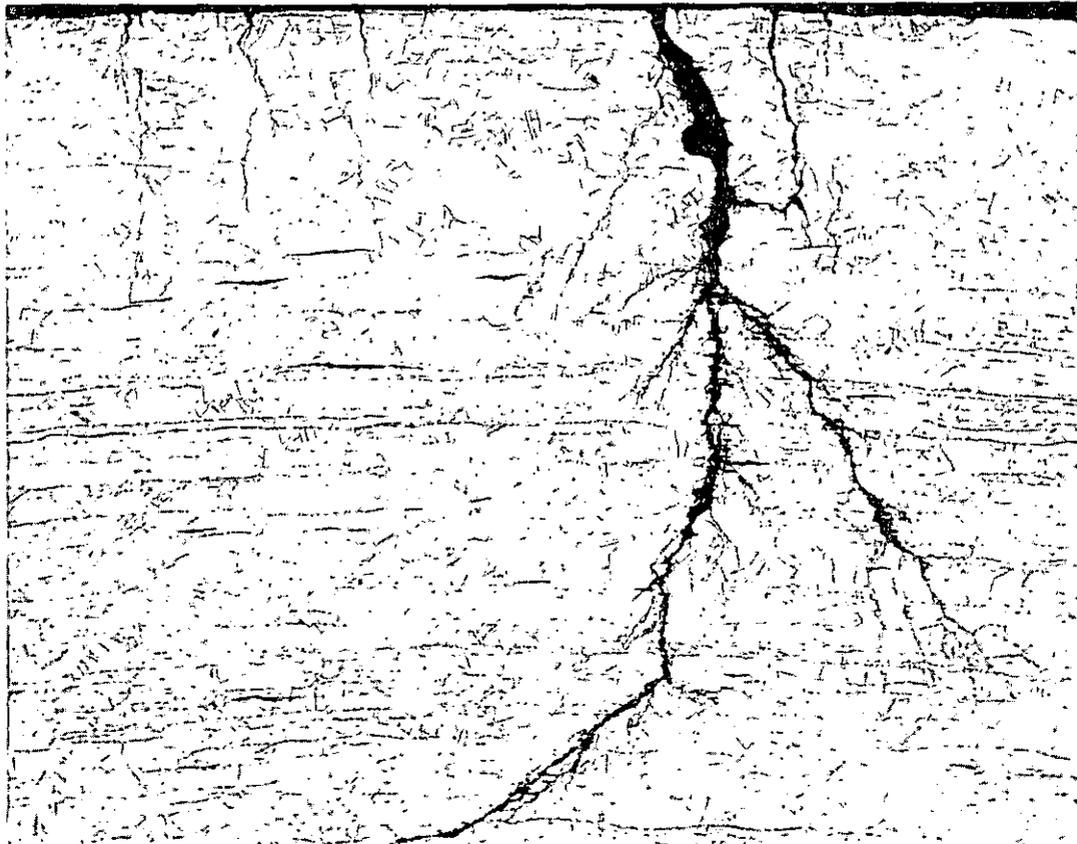
FIGURE 6. SECTION THROUGH CORROSION PIT IN TYPE 304 STAINLESS STEEL U-BEND SAMPLE. This sample was exposed 416 hours in boiling 42% $MgCl_2$ inhibited with 10% $NaNO_3$. There was no evidence of chloride stress corrosion cracking. Pit depth was 0.0016 inch.

UNCLASSIFIED



Approx 5X

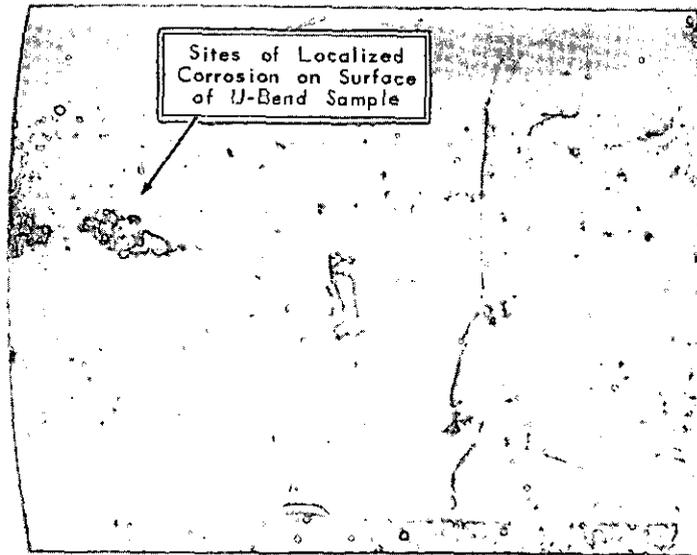
Neg EA-5581-A



Approx 100X

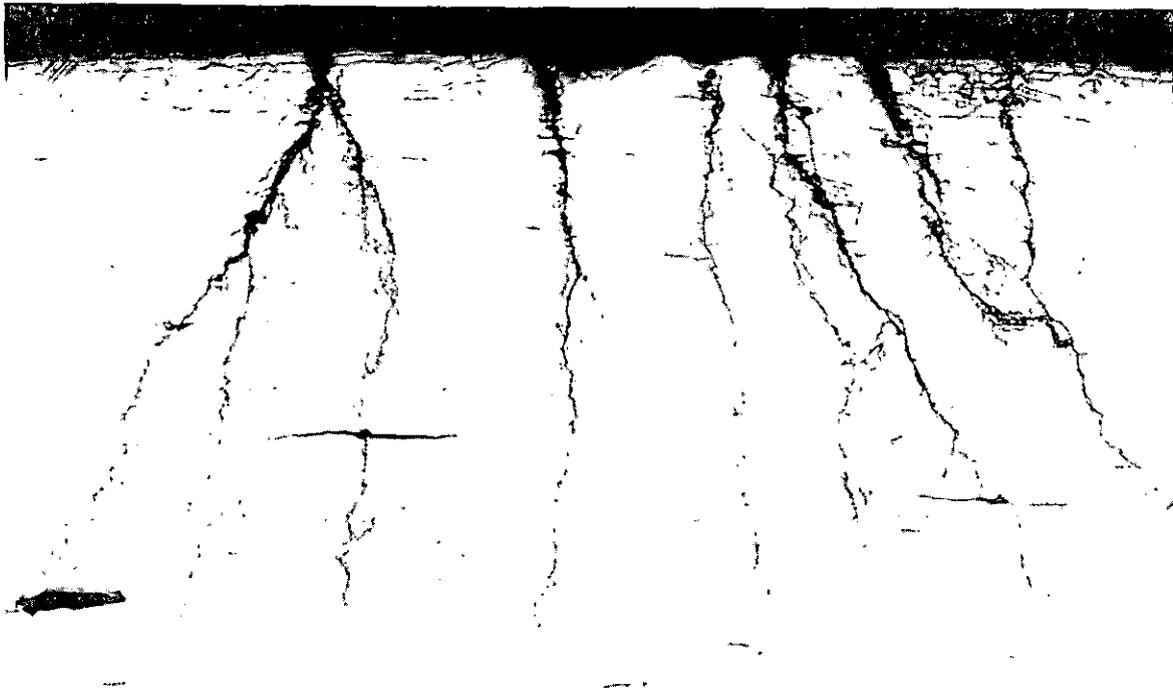
Neg EA-6959-A

FIGURE 7. PROPAGATION OF EXISTING CRACKS EVIDENCED BY CORROSION. Sample was initially cracked in boiling 42% $MgCl_2$, then exposed 310 hours in boiling water containing 100 ppm Cl^- (as $NaCl$). Section was through corrosion product buildup.



Approx 5X

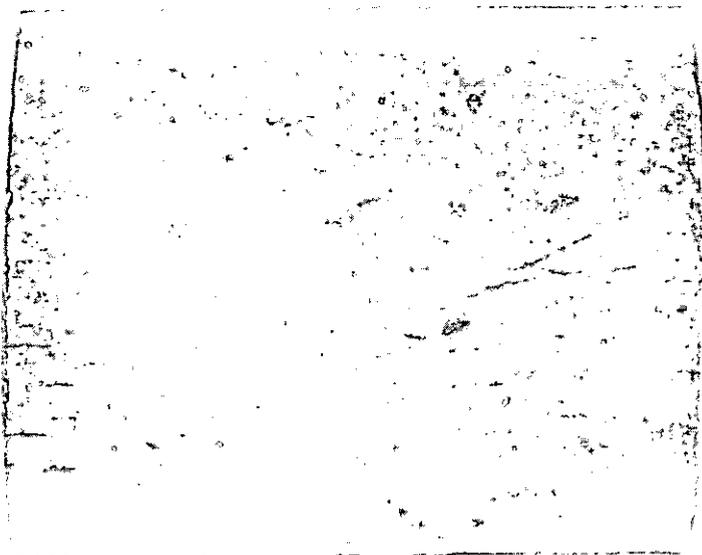
Neg EA-5624-A



Approx 150X

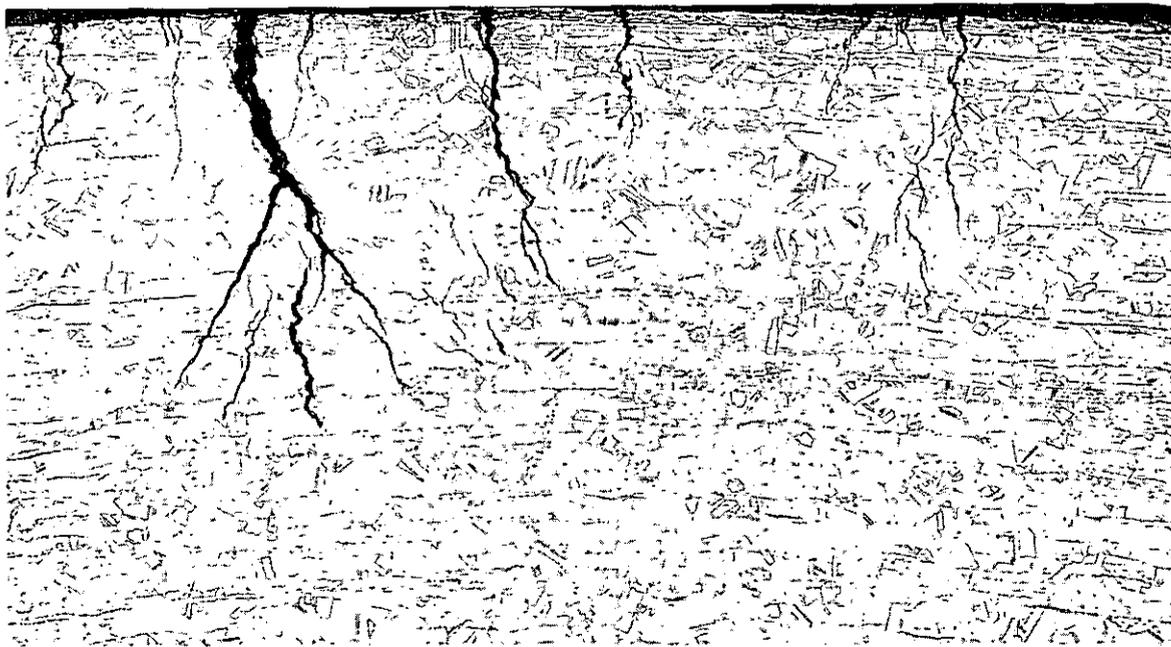
Neg EA-5625-A

FIGURE 8. LOCALIZED CORROSION AND CHLORIDE STRESS CRACKING ON TYPE 304 STAINLESS STEEL U-BEND SAMPLE. This sample was suspended 310 hours in the vapors above a boiling water solution containing 100 ppm Cl⁻.



Approx 5X

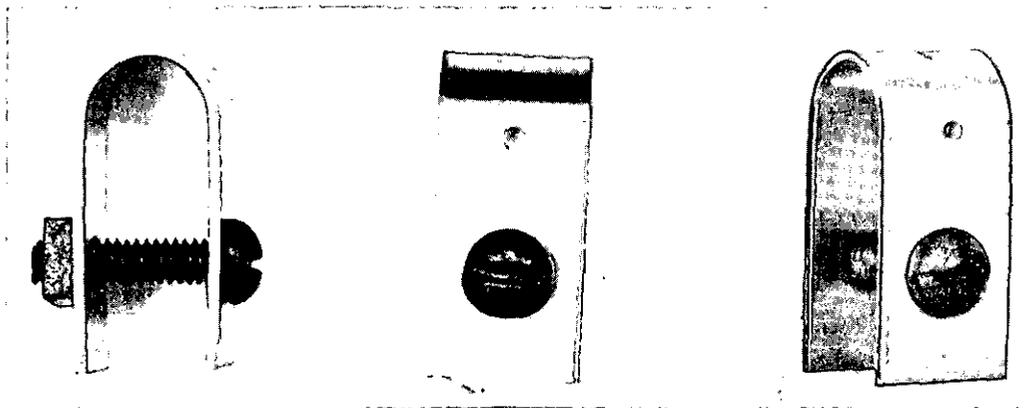
Neg EA-5587-A



Approx 100X

Neg EA-6964-A

FIGURE 9. CRACKED TYPE 304 STAINLESS STEEL U-BEND SAMPLE EXPOSED 2414 HOURS IN BOILING DISTILLED WATER. Sample was cracked initially in boiling 42% $MgCl_2$. Note metallographic section shows some widening of existing crack but no propagation.



Approx 1X

Neg EA-5650-A

FIGURE 10. TYPE 304 STAINLESS STEEL U-BEND SAMPLES COUPLED WITH CARBON STEEL BOLTS AFTER 638 HOURS IN 10 WT % NaNO_3 . Note staining of carbon steel bolts. Corrosion rate of the carbon steel was approximately 0.00035 inch per month.