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FACTORS CONTROLLING CHLORIDE STRESS CORROSION OF TYPE 304 STAINLESS STEEL*

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INTRODUCTION

The purpose of this paper is to describe circumstances that have caused chloride stress corrosion cracking of stainless steel equipment at the US-AEC Savannah River Plant, and to discuss both plant and laboratory investigations of methods for prevention and control of stress corrosion damage. Metallurgical factors that determine the degree of susceptibility to cracking for a given steel are not discussed in this paper.

Twenty years ago chloride stress corrosion cracking of austenitic stainless steel was considered by many people to be an interesting scientific phenomenon that occurred very rarely in practice and only under highly specific circumstances.(1,2) Today, however, this phenomenon is recognized as a major cause of damage to industrial equipment.

Innumerable cases of cracking have been described in the literature and considerable research has been devoted to studying the mechanism of stress corrosion cracking. The phenomenon has been the subject of several symposiums,(2-4) and some excellent survey papers and reports have recently appeared.(5-7) In spite of the vast amount of detailed information that has been developed there is still no general acceptance of any one of the various theories on the mechanism of stress corrosion cracking. This

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situation is not surprising in view of the complex interactions of metallurgical and chemical environmental factors that affect stress corrosion cracking.

Even if general agreement could be reached on the mechanism, this would not bring an end to stress corrosion damage of industrial equipment, particularly in plants where it is impractical to replace all crack-susceptible materials of construction or to make major changes in the processes. In such cases a consciencious program of inspection and preventive maintenance is required to locate sites of damage and wherever possible to apply protective measures to inhibit stress corrosion.

In the cases of cracking that will be described, the circumstances were not unique to the atomic energy field and could exist in a wide variety of industrial installations.

EXAMPLES OF EQUIPMENT DAMAGE

Type 304 stainless steel is used extensively at the Savannah River Plant throughout the nuclear reactor complex and in much of the chemical separations process equipment. A number of cases of stress corrosion cracking have occurred. Damage has occurred most frequently by the transgranular form of cracking in heat exchangers and in various sections of process piping. An unusual form of intergranular cracking that occurred in sensitized steel in contact with high-purity heavy water containing only about 0.02 ppm chloride ion was described in a previous paper.(8)

In all of the cases of cracking experienced at the Savannah River Plant, some mechanism had existed for concentrating chlorides on the steel surface. Only residual stresses from fabrication or assembly fit-up were involved, but these probably ranged from low levels up to the yield stress. Metal temperatures were mostly in the range of 50-100°C. Oxygen was present in every case.

Cracking under Insulation, Seals, and Labels

Numerous cases of cracking have occurred where chlorides were concentrated on the steel as a result of atmospheric moisture leaching soluble chlorides from thermal insulation, plastic identification bands, painted labels, and sealing materials. Several examples are illustrated in Figures 1 through 3.

Cracking beneath wet insulation has been described in detail by Dana.(9) This problem has been experienced in many plants and is not peculiar to the Savannah River Plant. Most failures occurred where operating temperatures were between 80 and 120°C. However, some failures occurred where the normal operating temperature was as low as 33°C. While soluble chlorides exist in most of the common insulating materials, the worst offender is 85% magnesia insulation. The well-known "wick test" developed by Dana and DeLong(10) is used to determine the tendency for a given kind of insulation to cause cracking when wetted.

Cracking under polyvinyl chloride plastic identification bands and painted labels on process piping occurred where operating temperatures were above 70°C. At locations where pipes pass through concrete radiation shielding, (Figure 2) chlorides leached from neoprene coatings used to seal the opening caused cracking at temperatures as low as 50°C. The use of plastic bands and painted labels has been discontinued, and neoprene seals have been replaced with chloride-free polyurethane.

Cracking under insulation, labels, and seals on pipe runs has caused a minimum amount of down time, and repair is usually inexpensive. The most costly and troublesome stress corrosion cracking problems at the Savannah River Plant have occurred in heat exchangers.

Cracking of Heat Exchanger Tubes and Parts

Savannah River Plant reactors are closed systems through which high-purity heavy water is circulated as moderator and coolant. Heat exchangers in the systems (illustrated in Figure 4) are of the shell-and-tube design, fabricated from types 304 and 304L stainless steel. They are 33' 6-1/2" long by 7' 4-1/2" in diameter. They operate with heavy water on the tube side and Savannah River cooling water on the shell side flowing countercurrent. Each heat exchanger contains 8957 1/2-inch OD x 18 BWG type 304 stainless steel tubes and is provided with a double tube sheet at both ends. The shell is fabricated from type 304L stainless steel and is welded to the 304L stainless steel inner tube sheets. Tubes are rolled into the four tube sheets, and the tube ends are welded to the outer tube sheets. The spaces between the inner and outer tube sheets are enclosed by carbon steel rings which slide into position against the outer tube sheet and are sealed by elastomer gaskets. The heat exchanger heads are held in position and reinforced by staybolts (type 303 stainless steel) screwed into the outer tube sheet. Details are shown in Figure 5. The double tube sheet design provides a "leak collection" space to prevent mixing of heavy and light water should a leak develop between the tubes and tube sheets. Leakage of heavy water into this space was detected in several heat exchangers after about 4-1/2 years operation.

Inspections revealed that stress corrosion cracking had occurred in many tubes in the leak collection spaces at the inlet ends of the heat exchangers. The cracks originated on the air side of the tubes. Some were visible to the eye while others were revealed by dye-penetrant inspection, as shown in Figure 6. The tube surfaces were covered by rusty corrosion products, some of which may have fallen off of the carbon steel rings. These corrosion products contained 300 ppm chloride ion by analysis. The chloride could have come either from the elastomer seal gasket (which contained 8% chloride) or from leakage of river water (2-9 ppm chloride) through the rolled joint between the tube and inner tube sheet. Severely cracked tubes were replaced, but less seriously damaged tubes were left in service to avoid costly shutdowns.

In order to minimize further stress corrosion damage of the tubes, the space between the double tube sheets was made part of a closed, recirculating liquid inhibitor system. The system was designed to protect tubes in leak collection spaces at both ends of all heat exchangers.

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. Based on the work of Williams,(11) and of Phillips and Singley,(12) alkaline sodium phosphate water with sodium sulfite added to scavenge oxygen was chosen for use in the inhibitor system. The solution composition was 1400-1600 ppm PO_4^{-3}, 50-100 ppm SO_3^{-2}, 2000 ppm (max) SO_4^{-2}, and pH 10.5 to 11.0. Laboratory tests, described later, were performed to confirm that this solution would inhibit propagation of existing cracks.

This inhibitor system has operated successfully for about 4 years. Propagation of existing cracks has been prevented, thereby enabling continuation of operation without replacement of all cracked tubes.

Cracking has occurred at other locations in these same heat exchangers. When the heads were removed to replace failed tubes, rust-type corrosion products and cracks were observed on many staybolts and O-ring seal surfaces in the head bosses. A cracked staybolt is shown in Figure 7. Chlorides were leached from the rubber O-rings either by condensate or water leakage. All cracked staybolts were replaced, and O-rings were eliminated by changing to a welded staybolt closure.

Cracking has also occurred in the rolled area of the tube-to-inner-tube-sheet joint nearest the river water side. Cracking of the tubes at this location was not associated with cracking in the leak collection space because many tubes that cracked under the inner tube sheet were not cracked in the leak collection space. In these cases, either residual chlorides from initial fabrication or cleaning were trapped in the rolled joint, or chlorides in the river water concentrated in the crevice.

The experiences with chloride stress corrosion cracking described above involved equipment worth many millions of dollars. Fortunately, remedial actions to repair damage and arrest crack propagation have been successful. However, unanticipated cases of cracking continue to occur sporadically. In view of this and the lack of general agreement on the mechanism of cracking, a program of laboratory studies of stainless steel stress corrosion was begun.

LABORATORY STUDIES

The major objectives of laboratory studies to date have been to investigate methods of inhibiting cracking of a susceptible steel and to investigate the effects of chemical-environmental factors, especially pH, on stress corrosion cracking.

Some of the results of studies on the effects of pH were described in a previous paper.(13) That work demonstrated that the cracking behavior of type 304 stainless steel is fundamentally related to pH. The effects of pH will be discussed later in greater detail.

Some information on inhibiting cracking has appeared in the literature. For example, Uhlig and Lincoln(14) reported that cathodic polarization with current densities of 3×10^{-5} amp/cm^2 prevented cracking during a 24-hour test in boiling 42% $MgCl_2$. Phillips and Singley(12) reported that in autoclave tests, sodium nitrate inhibited cracking if the mole ratio of nitrate to chloride ion was at least one and the pH of the chloride solution was higher than about 10.5.

The present work sought answers to the following questions:

1. Does cathodic protection with either impressed current or sacrificial anodes inhibit cracking in boiling 42% $MgCl_2$ for extended exposures?
2. Does the nitrate ion inhibit cracking in various concentrated chloride solutions without alkaline pH control?
3. Do inhibitors that prevent initiation of cracks also prevent propagation of cracks formed prior to exposure to the inhibited chloride solutions?
4. Do existing cracks propagate when moisture is driven off but solid chloride salt remains; or when chlorides are removed and samples are submerged in pure boiling water or in steam, or heated in dry chloride-free air?
5. What is the relative importance of chloride ion concentration versus pH effects on stress corrosion cracking in aqueous chloride solutions?

Experimental Techniques

U-bend samples stressed to plastic yield were used in all tests. Stresses in this type of sample are complex,(15) and for this reason U-bend samples may be unsuitable for fundamental studies in which stress is a primary variable. However, in this work U-bend samples were appropriate because they simulate the complex situation that exists in most industrial equipment. For example, in heat exchangers the tubes have cold-worked areas in the region of the tube sheets, and stresses probably cover a broad range up to the yield stress.

The samples were cold formed from 3-1/2- x 3/4-inch strips, which had been sheared from 16-gage mill-annealed sheet. They were not heat treated or surface ground. All samples were thoroughly washed and degreased prior to testing. Type 304 stainless steel was used in all cases except for one series of tests noted later in which type 304L stainless steel was used. The heat analyses of these steels are given in Table I. Type 304 stainless steel nuts and bolts (not insulated) were used to stress the samples. Samples used in tests to determine if existing cracks propagate were first exposed to boiling 42% $MgCl_2$ for 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 8.

Tests were performed in wide-mouth Erlenmeyer flasks fitted with "cold finger" condensers to prevent loss of evaporation. Propagation of existing cracks was detected by careful visual inspection and metallographic sectioning. Crack propagation in dilute solutions invariably produced a rusty corrosion product on the sample surface.

Tests in Alkaline Phosphate-Sulfite Solution for Plant Use

Tests were performed to determine if propagation of existing cracks would be prevented by the alkaline sodium phosphate-sulfite solution selected for use in the heat exchanger inhibitor system. Tests were run with and without a nitrogen blanket to protect against loss of sulfite by reaction with oxygen in air. Chloride ion concentrations (as NaCl) were 100 ppm or <0.1 ppm.

Results are summarized in Table II. No crack propagation was detected in any of the tests, indicating that at these low levels of chloride concentration the alkaline phosphate solution even without residual sulfite was sufficient to inhibit crack propagation.

Cathodic Protection Tests in Boiling 42% $MgCl_2$

Results of these tests are presented in Table III.

Cathodic protection provided by zinc or aluminum washers attached to the legs of the U-bend samples prevented cracking (and propagation of existing cracks), if electrical contact was not broken by the accumulation of corrosion products or the anode was not completely corroded away. Both zinc and aluminum corroded severely in the boiling 42% $MgCl_2$.

A cathodic current of 10^{-4} amp/cm^2 prevented cracking and propagation of existing cracks for exposure times up to 129 hours. A cathodic current of 10^{-5} amp/cm^2 was insufficient protection and samples cracked within 1-1/2 hours. These data are in good agreement with Uhlig and Lincoln,(14) who reported 3×10^{-5} amp/cm^2 prevented cracking during a 24-hour test.

Nitrate Ion Inhibitor Tests in Concentrated Chloride Solutions

Results of these tests are presented in Table IV.

Type 304L samples were tested in three different chloride solutions containing various nitrate salts. Boiling solutions of 42% $MgCl_2$, 45% $MnCl_2$, and 19% $FeCl_2$ + 18% $FeCl_3$ were tried. The latter was highly acid and corroded the samples severely. Cracking in 45% $MnCl_2$ was nearly as severe as in 42% $MgCl_2$, but samples were slightly more corroded by the 45% $MnCl_2$.

Additions of 5 wt % of various metal nitrates tended to inhibit cracking, but complete protection was obtained only in 45% $MnCl_2$ containing nitrates of lead, zinc, tin, or sodium.

Type 304 stainless steel samples were tested in boiling 42% $MgCl_2$ containing sodium nitrate additions of 1, 5, and 10%. Cracking occurred in the 1 and 5% solutions but the addition of 10% sodium nitrate inhibited cracking and propagation of existing cracks in tests of 584 hours duration. Some slight pitting occurred, but metallographic sections through pits confirmed that there was no cracking.

Tests in Dilute Aqueous Solutions

Results of these tests are presented in Table V.

Type 304 stainless steel samples initially cracked in 42% $MgCl_2$ were washed thoroughly and then exposed along with uncracked samples in boiling distilled water at pH 5.5 and containing 100 ppm chloride ion (as NaCl), and in the same solution inhibited with 10% sodium nitrate (pH 6.0). Cracked and uncracked samples were also suspended above the solutions such that the condensate dripped onto the tensile-stressed surface of the U-bends. Analyses of condensate were 1.0 to 1.5 Cl^- in both cases, and 0.5 to 1.0 ppm NO_3^- in the condensate from the inhibited solution.

With no inhibitor present, cracking and propagation of existing cracks occurred both in immersed and suspended samples. Also, stainless steel wires used to suspend the samples in the vapor phase were cracked after 929 hours. These results were surprising because of the low chloride levels and relatively low temperatures (about 80°C in vapor and 100°C in solutions). Also, the wires were subjected to only residual stresses plus the weight of the samples. Cracking in the vapor phase was probably stimulated by the abundance of oxygen. Cracking and/or propagation of existing cracks was always evidenced by a visible rusty corrosion product buildup. Figure 9 illustrates this on a sample that was immersed in 100 ppm Cl^- solution after being initially cracked in 42% $MgCl_2$. The sites of active corrosion and crack propagation are evident. Initially uncracked samples developed rust spots along the sheared edges, and metallographic sectioning confirmed cracking had occurred.

The addition of 10 wt % sodium nitrate to water containing 100 ppm Cl^- prevented cracking and stopped the propagation of existing cracks in both immersed and suspended samples. The fact that no cracking occurred in wires or samples in the vapor phase indicates that a concentration of sodium nitrate considerably less than 10% would probably inhibit cracking in dilute chloride solutions. The effectiveness of lower concentrations of sodium nitrate was not investigated in the present work.

Tests of Crack Propagation in Dry or Chloride-Free Environments

Samples initially cracked in 42% $MgCl_2$ were tested along with uncracked control samples in the following environments:

Hot dry air (170-200°C)
Pure dry sodium chloride (90°C)
Boiling distilled water (100°C, <1 ppm Cl^-)
Steam [200 psig (197°C); 300 psig (216°C)]

Results are presented in Table VI.

No cracking or crack propagation occurred in dry air or dry sodium chloride, although in both cases existing cracks were oxidized.

Exposures up to 2414 hours in boiling distilled water caused only slight staining of the surface around existing cracks. Metallographic sectioning revealed slight yawning and oxidation of existing cracks but no propagation. Samples exposed in steam were slightly oxidized but no cracking occurred (no alternate wetting and drying to concentrate chlorides).

Importance of Chloride Concentration Versus pH

Tests were performed to determine the relative importance of chloride ion concentration and pH effects on stress corrosion cracking of type 304 stainless steel. Stressed U-bend samples were exposed in boiling solutions of distilled water containing chloride ion concentrations of 100 ppm, 33,000 ppm, and 100,000 ppm, and pH adjustments in a range of 0 to 10. In solutions of 33,000 ppm and 100,000 ppm Cl^-, pH was adjusted with HCl or NaOH. In the 100 ppm Cl^- solutions HNO_3 or NaOH was used because addition of HCl to increase acidity below about pH 3 would have raised the chloride ion concentration above 100 ppm.

Previous tests using samples cold-formed from mill-annealed sheet had shown that cracks frequently initiated at cold-worked areas (edges) and did not propagate to the extent that complete rupture of the U-bend sample occurred. Therefore, time-to-fracture was not a good criterion for rating cracking tendency. However, rusty corrosion products always appeared at crack sites (above pH 3), indicating that corrosion rates calculated from weight loss plus visual and metallographic examinations would be good criteria for rating the cracking behavior. Results obtained using these criteria are presented in Figures 10, 11, and 12.

These tests demonstrated that pH exerts a very strong influence on stress corrosion cracking over a wide range of chloride ion concentrations. In solutions containing 100 ppm Cl^- (Figure 10), cracking occurred over the range of pH 3.5 - 8.0. Cracks were generally very small, originated at sheared edges, and propagated very little. No cracking occurred at pH 10, or in any solutions in the acid range below pH 3.0. Similar effects occurred in solutions containing 33,000 ppm Cl^- (Figure 11), except that cracking was more severe and occurred over the range 4 - 10. Increasing the chloride ion concentration to 100,000 ppm (10%) still did not cause cracking in solutions more acid than about 3.5 - 3.0 or less, as shown in Figure 13.

Corrosion by pitting and general attack increased rapidly in acidic solutions adjusted with HCl. Metallographic examination of samples exposed in 33,000 ppm and 100,000 ppm chloride solutions in the acid region revealed a tendency for transgranular cracks to form, but cracks never penetrated deeper than the numerous pits which extended only about 0.005 inch below the surface suffering general attack. In acidic solutions adjusted with HNO_3, passivity was retained because of the oxidizing nature of the acid, and the chloride concentration (100 ppm) evidently was too low to cause breakdown of passivity.

The general shape of the corrosion rate versus pH curves is consistent with previous studies of pitting corrosion of austenitic stainless steel in salt water.(16)

The effect of pH on corrosion rate can be explained on the basis of corrosion product solubilities. In non-oxidizing acidic solutions the chemical reactions by which corrosion occurs yield products that are very soluble. As the acidity decreases, the products become predominantly insoluble. Adherence of insoluble products on the surface promotes passivity and reduced corrosion rates. In nitric acid, passivity is retained because of the strongly oxidizing nature of the solutions. The fact that stress corrosion cracking occurred only in the pH range where the steel tended to develop passivity supports the theory that cracking occurs by highly localized electrochemical corrosion. In the pH range where cracks developed the only significant corrosion occurred at the crack sites.

Previous work(13) demonstrated that in sensitized type 304 stainless steels the path of cracking in low-chloride water was strongly influenced by pH. Cracking was predominantly transgranular in the pH range of 4-7, but became entirely intergranular in the pH range of 3.0-3.5. When the acidity was increased with nitric acid below pH 2.5, general intergranular corrosion occurred with no evidence of localized crack-like penetrations. These effects were also consistent with the theory that cracking occurred by highly localized corrosion in steel that tended to develop passivity. The change from predominantly transgranular to entirely intergranular was explained on the basis that in slightly acidic solutions the grain boundaries tended to remain active and represented the most susceptible corrosion path. In the neutral solutions the stronger tendency towards passivation caused grain boundaries to become less active so that cracking then was either intergranular or transgranular (or mixed) depending entirely on where the corrosion cell became localized.

There is overwhelming evidence that initiation of stress corrosion cracking occurs as a result of highly localized electrochemical corrosion. The mechanism of crack propagation remains in doubt. Localized anodic dissolution (perhaps accelerated by mechanical yielding along the crack tips) may be entirely responsible for cracking. On the other hand, the role of corrosion may be to create a specific surface condition that drastically reduces the yield strength (chemisorption theory) so that crack propagation is accelerated by mechanical yielding. Still another possibility is that corrosion-produced hydrogen is involved in crack propagation, either by reaction with the steel producing a brittle and corrosion-susceptible phase,(17) or by being absorbed into the steel and causing local embrittlement. Research is continuing to determine how cracks propagate and how metallurgical structure and composition affect susceptibility to stress corrosion cracking.

CONCLUSIONS

The practical experience and laboratory studies described in this paper shows that electrochemical corrosion plays the dominant role in chloride stress corrosion cracking of type 304 stainless steel. Experience has shown that the chloride content of the environment is of little importance if some mechanism exists for concentrating chlorides on the steel surface. The rate at which stress corrosion damage occurs increases with increasing chloride content and corrosiveness of the environment and increasing stress levels. At low stress levels (residual or applied) cracking occurs slowly as chlorides become concentrated and local corrosion cells are generated. Damage to equipment can be prevented or minimized by a conscientious program of inspection and application of inhibiting techniques.

The strong influence of pH on cracking behavior in laboratory studies supports the theory that stress corrosion cracking occurs by localized electrochemical corrosion.

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TABLE I

ANALYSES OF STAINLESS STEELS USED IN LABORATORY STUDIES

Element	Amount, wt %	
	Type 304	Type 304L
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

TABLE II

INHIBITING CRACK PROPAGATION WITH ALKALINE PHOSPHATE-SULFITE WATER*

Test No.**	Sample Location	Atmosphere	Cl^-, ppm	Temp, °C	Exposure Time, hrs	Result
1	Immersed in liquid	Nitrogen gas blanket	0.1	90	1478	No crack propagation
2	Immersed in liquid	Nitrogen gas blanket	100	90	1672	No crack propagation
3a	Suspended in vapors with condensate dripping on samples	Air and vapors	100	60-90	954	No crack propagation
3b	Immersed in liquid	Air and vapors	100	100 (boiling)	954	No crack propagation

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* PO_4^{-3} = 1400-1600 ppm
SO_3^{-2} = 50-100 ppm
SO_4^{-2} = 2000 ppm (max)
pH = 10.5 to 11.0

** 4 samples in each test.

TABLE III

CATHODIC PROTECTION TESTS IN BOILING 42% $MgCl_2$

Method of Cathodic Protection	No. and Type of Samples*	Time, hrs	Results
Zinc Washer, grams			
2.3	1 uncracked	20	Samples cracked after zinc corroded away
2.3	1 cracked	20	Samples cracked after zinc corroded away
4.9	1 uncracked	936	No evidence of cracking. Zinc was heavily corroded
5.8	1 cracked	936	No evidence of crack propagation. Zinc was heavily corroded
13.3	1 uncracked	936	No evidence of cracking. Gray film on sample
15.3	1 cracked	936	No evidence of crack propagation. Gray film on sample
Type 2S Al Washer, grams			
0.6	1 uncracked	547	Sample cracked after Al corroded away
0.6	1 cracked	547	Sample cracked after Al corroded away
1.4	1 uncracked	817	No evidence of cracking. White film on sample
1.3	1 cracked	817	No evidence of crack propagation. White film on sample
Type B605 Al (Al + 5% Zn) Washer, grams			
1.2	2 uncracked	338	Samples cracked after washer corroded away
0.9	2 cracked	235	Samples cracked after washer corroded away
Impressed Current, amp/cm^2			
10^{-5}	2 uncracked	1.5	Samples cracked
10^{-4}	2 uncracked	129	No evidence of cracking. Surface film.

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* Samples designated "cracked" were exposed 1 hour in boiling 42% $MgCl_2$ to produce cracks prior to start of this test.

TABLE IV

NITRATE ION INHIBITOR TESTS IN CONCENTRATED CHLORIDE SOLUTIONS

Type Steel	Solution	Time, hrs	Results	
			Stress Cracking	General Corrosion
304L	42% $MgCl_2$	61	Very severely cracked	Slightly stained
	42% $MgCl_2$ + 5% $Cu(NO_3)_2$	61	Cracked, not broken	Slightly corroded
	42% $MgCl_2$ + 5% $Pb(NO_3)_2$	61	Cracked, not broken	Slightly stained
	42% $MgCl_2$ + 5% $Zn(NO_3)_2$	61	Severely cracked	Slightly stained
	42% $MgCl_2$ + 5% $NaNO_3$	72	Many cracks, none penetrated	Slightly corroded
	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
	45% $MnCl_2$ + 4.7% $Mn(NO_3)_2$	72	No cracks	Slightly stained
	45% $MnCl_2$ + 5% $NaNO_3$	49	No cracks	Slightly stained
	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
304	42% $MgCl_2$ + 1% $NaNO_3$ (soluble)	1.5	Samples cracked	
	42% $MgCl_2$ + 1% $NaNO_3$ (soluble)	1.5	Cracks propagated	
	42% $MgCl_2$ + 5% $NaNO_3$ (NaCl precipitate)	15	Samples cracked	
	42% $MgCl_2$ + 5% $NaNO_3$ (NaCl precipitate)	15	Cracks propagated	
	42% $MgCl_2$ + 10% $NaNO_3$ (NaCl precipitate)	584	No cracking. Slight corrosion pitting	
	42% $MgCl_2$ + 10% $NaNO_3$ (NaCl precipitate)	584	No crack propagation. Slight pitting	

TABLE V

INHIBITING STRESS CORROSION CRACKING IN BOILING WATER CONTAINING 100 ppm CHLORIDE (AS NaCl)

Inhibitor	Conc, wt %	No. and Type of Sample	Time, hr	Remarks
None		4 (uncracked) immersed	310 (1) 1910 (3)	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)	
None		4 (cracked) immersed	310 (1) 1910 (3)	Heavy rust stains with corrosion and corrosion product buildup at some cracks. Metallography revealed crack propagation
None		4 (cracked) suspended in vapors (condensate dripping)	310 (1) 1910 (3)	
$NaNO_3$	10	4 (uncracked) immersed	256 (1) 1910 (3)	No corrosion or cracking
$NaNO_3$	10	4 (uncracked) suspended in vapors (condensate dripping)	256 (1) 1910 (3)	
$NaNO_3$	10	4 (cracked) immersed	256 (1) 1910 (3)	
$NaNO_3$	10	4 (cracked) suspended in vapors (condensate dripping)	256 (1) 1910 (3)	

TABLE VI

PROPAGATION OF EXISTING CRACKS

Environment	No. and Type of Samples	Temp, °C	Time, hr	Remarks
Dry Air	3 (cracked)	170 - 200	384	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	Oxidation in cracks. No propagation
Pure Dry NaCl	2 (uncracked)	90 - 95	310	No oxidation.
Boiling Distilled Water	12 (cracked)	100	2414	Very light stain around some cracks. No propagation.
Boiling Distilled Water	12 (uncracked)	100	2414	No cracks or corrosion.
Steam at 300 psig	6 (cracked)	216	144	Slate gray oxide on surface and in cracks. No propagation.
Steam at 300 psig	6 (cracked)	216	264	Same as above.
Steam at 200 psig	6 (cracked)	197	696	Same as above.
Steam at 200 psig	6 (cracked)	197	336	Slate-gray oxide on surface.

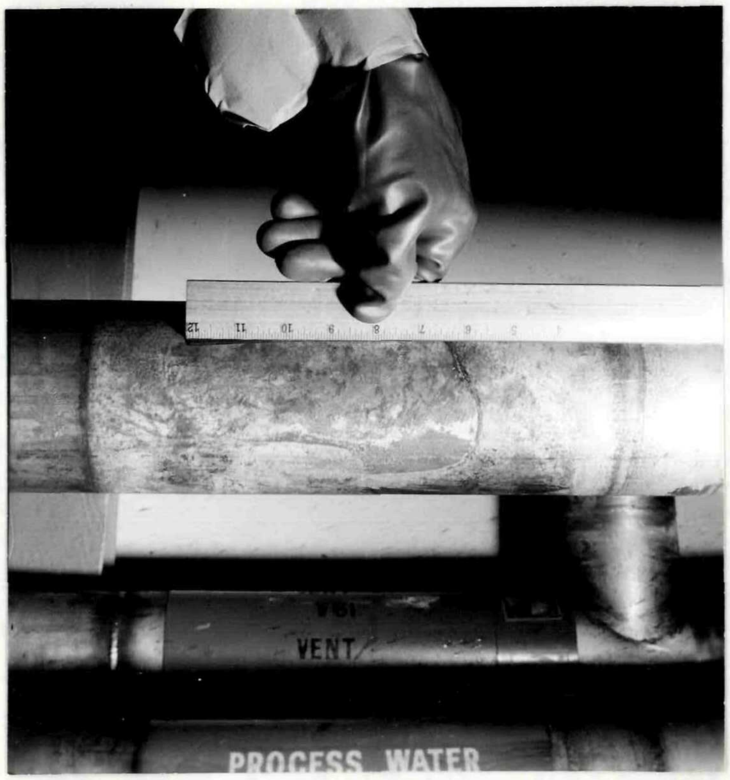


FIGURE 1. STRESS CORROSION UNDER LABELS. Atmospheric moisture concentrates chlorides under labels. Rusty corrosion products indicate beginning of attack. Careful inspection is required to detect cracks.

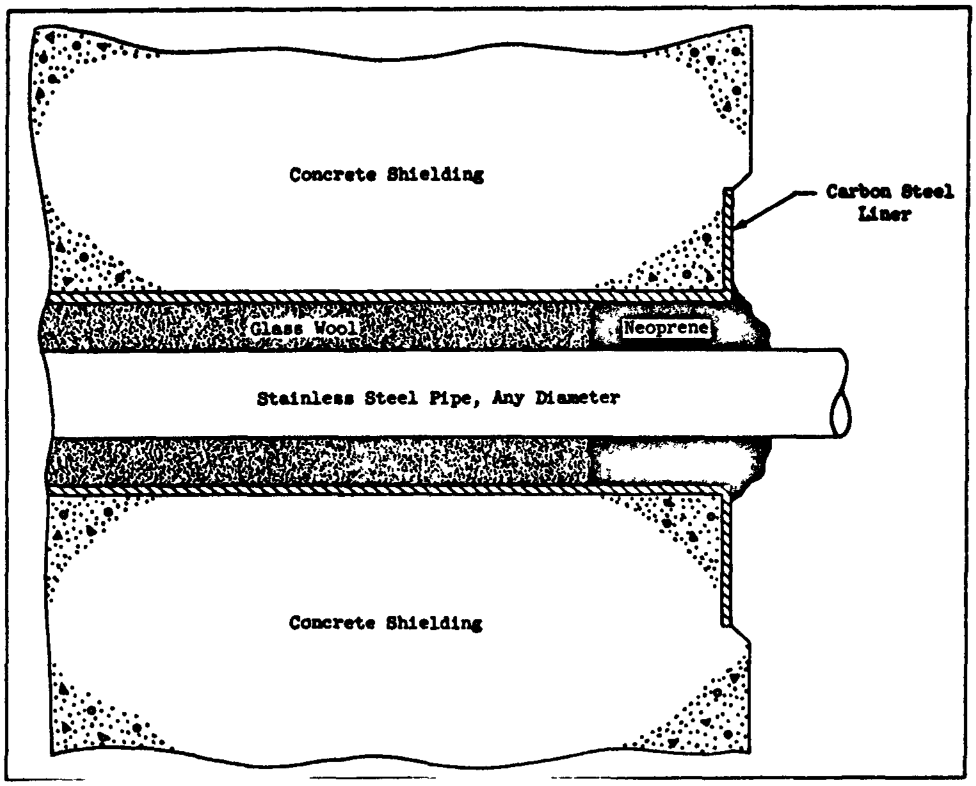


FIGURE 2. PIPE RUN THROUGH CONCRETE SHIELDING. Chlorides leached from neoprene seal caused severe stress corrosion cracking of pipe at 70°C.

Surface 5X

Cross Section 10X

FIGURE 3. STRESS CORROSION CRACKING OF TYPE 304 STAINLESS STEEL PIPE COATED WITH NEOPRENE. This is also typical of cracking found under painted and plastic labels.

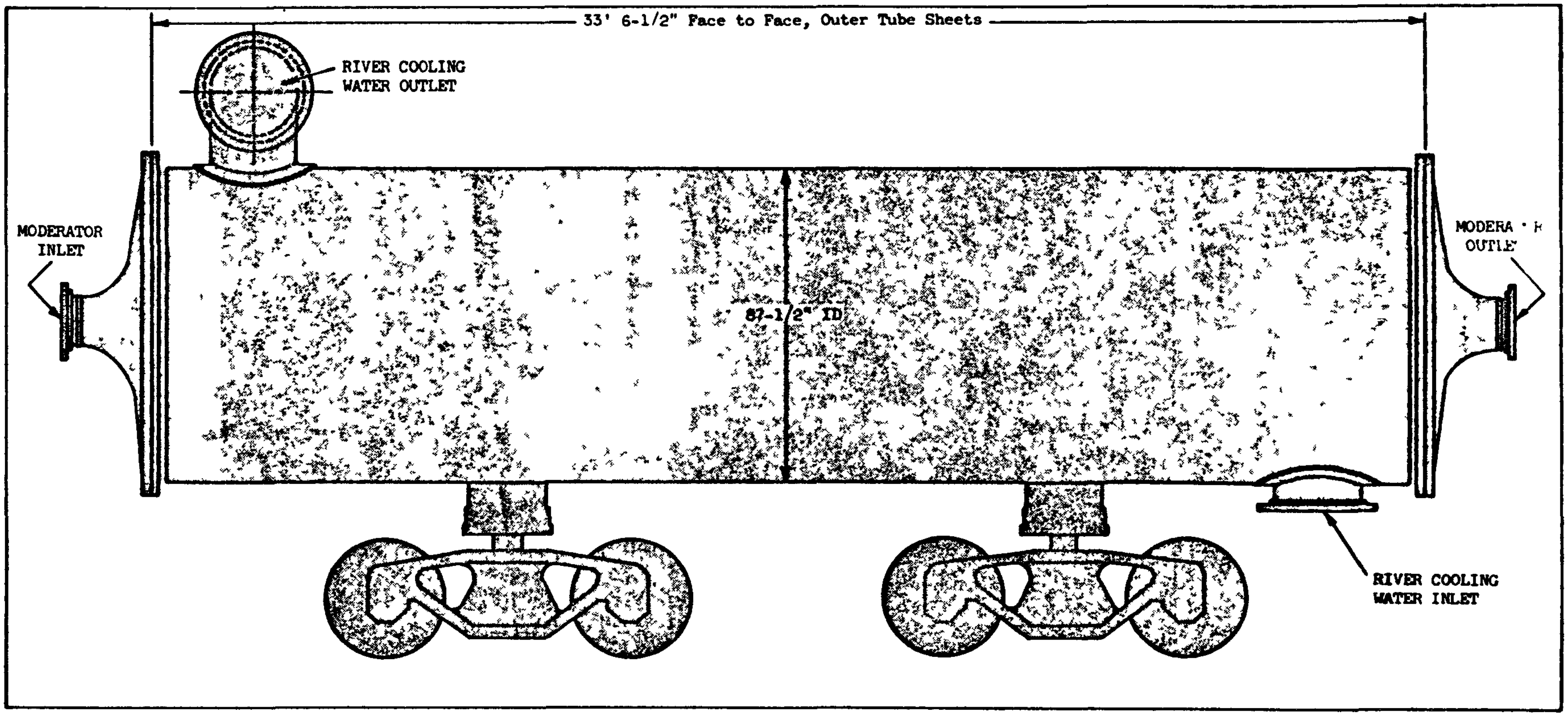


FIGURE 4. GENERAL ARRANGEMENT OF HEAT EXCHANGER

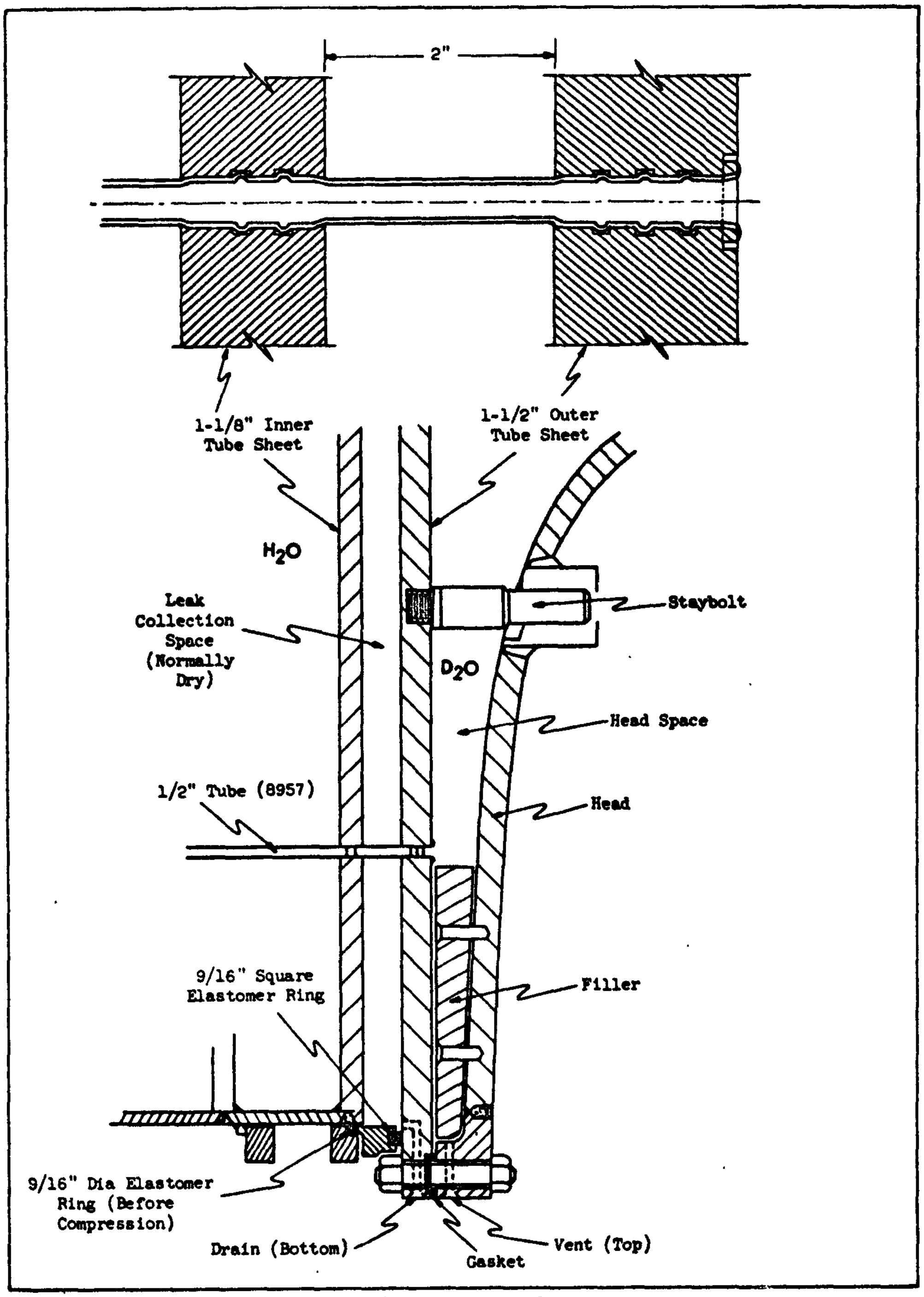
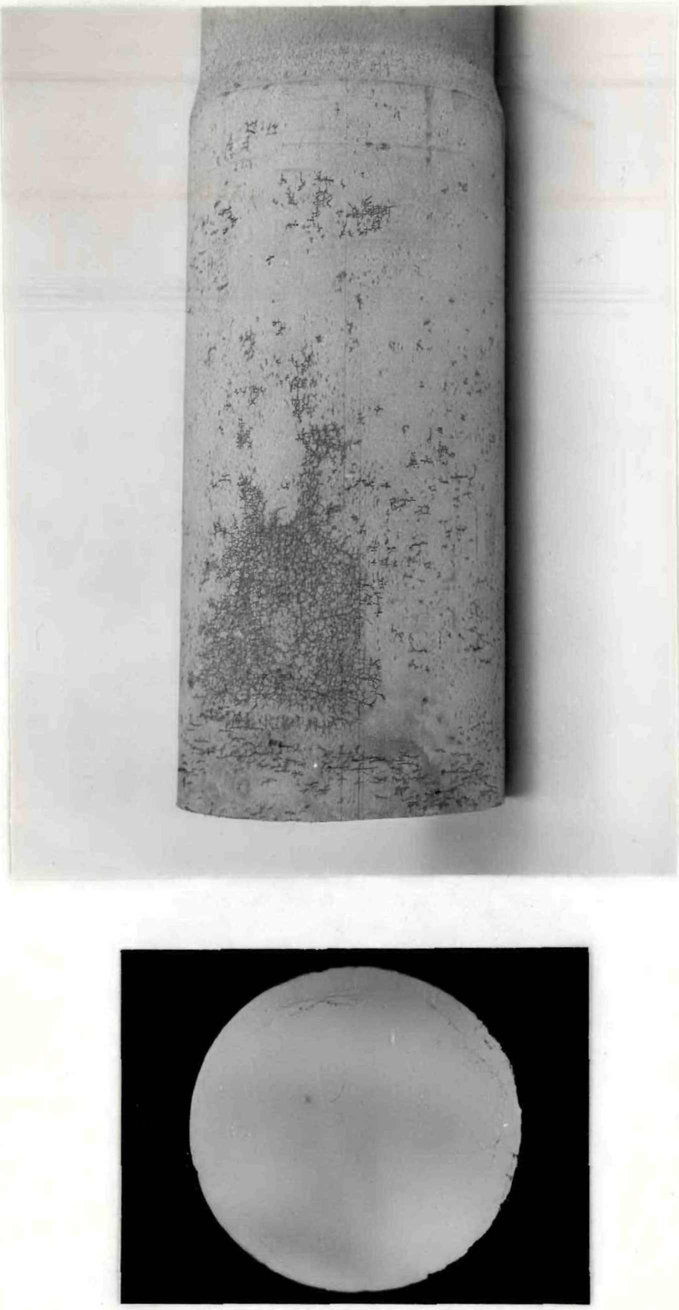


FIGURE 5. DETAILS OF LEAK COLLECTION SPACE AND DOUBLE TUBE SHEET

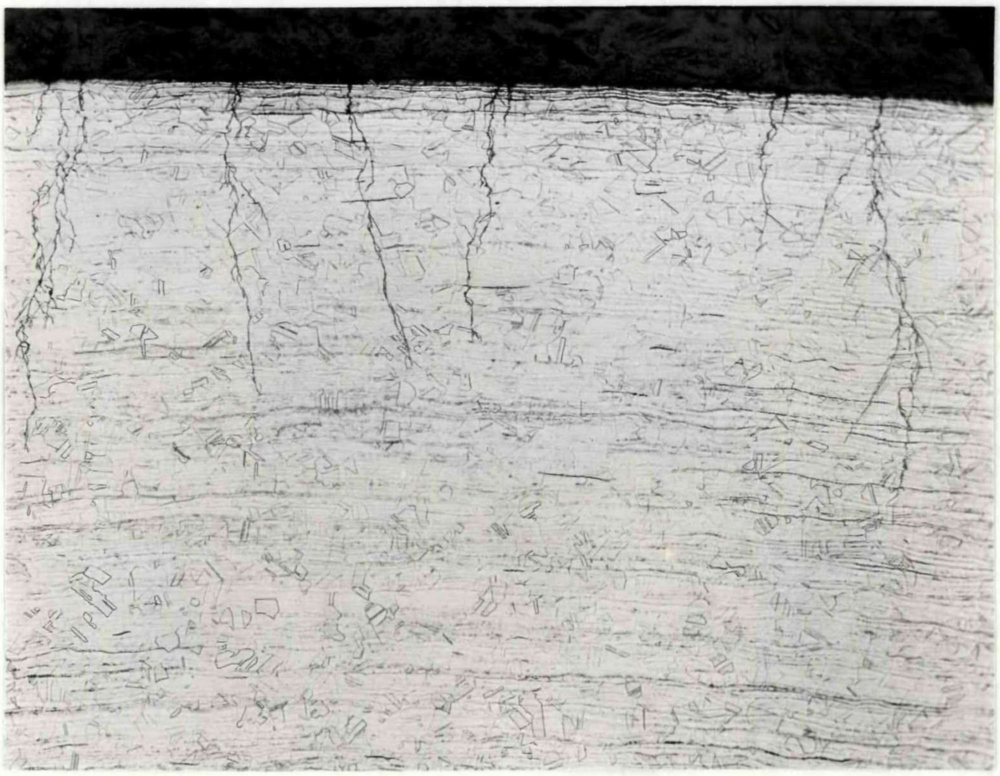
FIGURE 6. CRACKED TUBES IN LEAK COLLECTION SPACE REVEALED BY DYE PENETRANT TEST



Mag. $\sim$1X

FIGURE 7. STRESS CORROSION CRACKING OF HEAT EXCHANGER HEAD STAYBOLT. Cracking was caused by chlorides leached from O-rings.

5X



100X

FIGURE 8. STRESS CORROSION CRACKING OF TYPE 304 STAINLESS STEEL SAMPLE AFTER 1 HOUR IN BOILING 42% $MgCl_2$. Typical of samples used to study propagation of existing cracks.

5X

Initial
Crack
Depth

100X

FIGURE 9. PROPAGATION OF EXISTING CRACKS DURING TEST IN BOILING DISTILLED WATER CONTAINING 100 ppm Cl^-. Corrosion product buildup at active cracks.

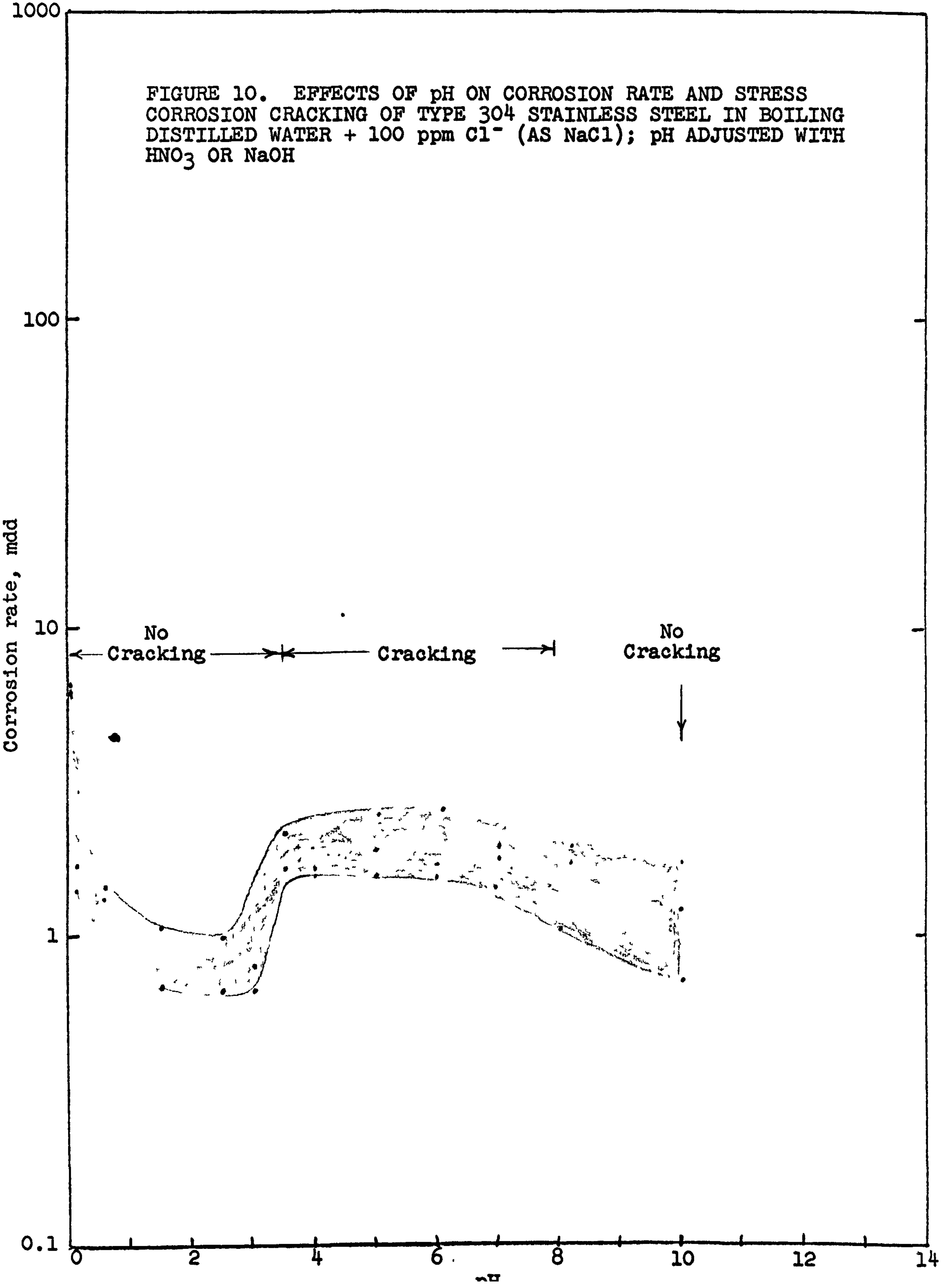


FIGURE 10. EFFECTS OF pH ON CORROSION RATE AND STRESS CORROSION CRACKING OF TYPE 304 STAINLESS STEEL IN BOILING DISTILLED WATER + 100 ppm Cl^- (AS NaCl); pH ADJUSTED WITH HNO_3 OR NaOH

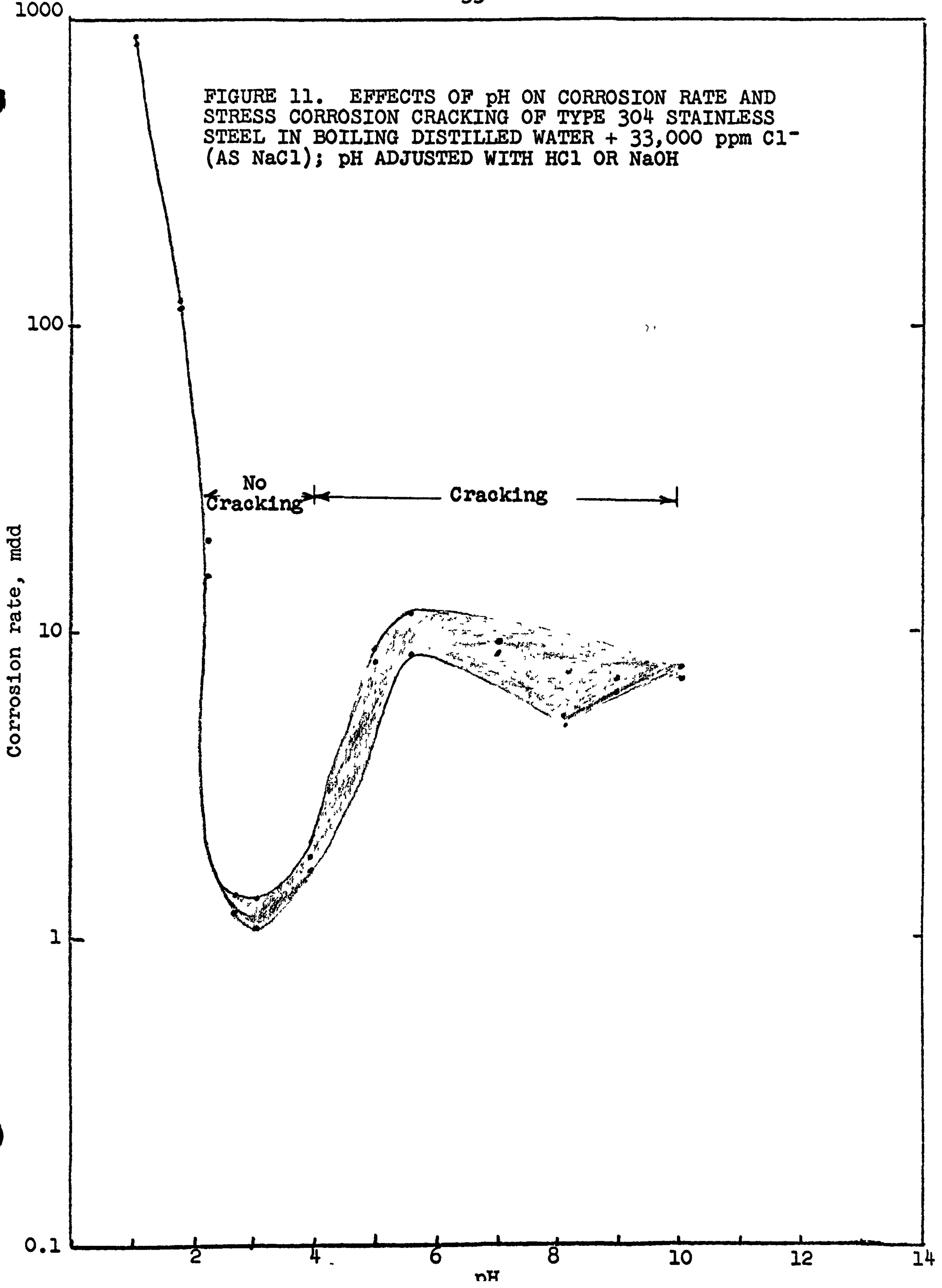


FIGURE 11. EFFECTS OF pH ON CORROSION RATE AND STRESS CORROSION CRACKING OF TYPE 304 STAINLESS STEEL IN BOILING DISTILLED WATER + 33,000 ppm Cl^- (AS NaCl); pH ADJUSTED WITH HCl OR NaOH

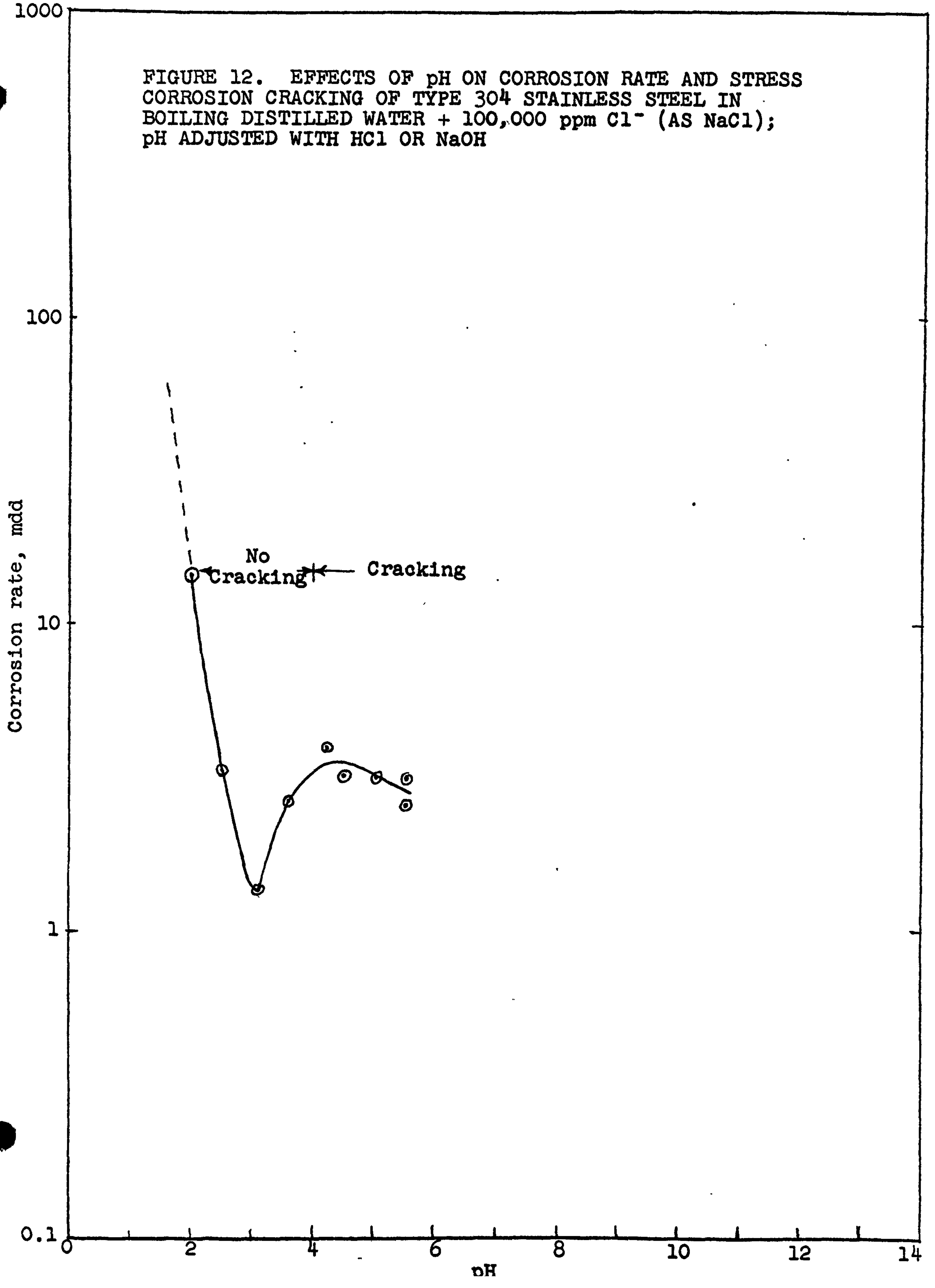


FIGURE 12. EFFECTS OF pH ON CORROSION RATE AND STRESS CORROSION CRACKING OF TYPE 304 STAINLESS STEEL IN BOILING DISTILLED WATER + 100,000 ppm Cl^- (AS NaCl); pH ADJUSTED WITH HCl OR NaOH