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THE EFFECTS OF ORGANIC ACIDS ON THE STRESS-CORROSION CRACKING OF TYPE 304 STAINLESS STEEL IN HIGH TEMPERATURE WATER

The Ohio State University

Ph.D. 1985

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THE EFFECTS OF ORGANIC ACIDS ON THE STRESS-CORROSION CRACKING OF TYPE 304 STAINLESS STEEL IN HIGH TEMPERATURE WATER

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree

Doctor of Philosophy in the Graduate School of the Ohio State University

By

Timothy Keane Christman, B.S., M.S.

The Ohio State University

1985

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iii.
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Studies in Thermodynamics, Dr. George R. St.Pierre

Studies in Solidification Processes, Dr. Carroll E. Mobley
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INTRODUCTION

Boiling water reactors (BWR) in the United States and Western Europe make extensive use of AISI Type 304 stainless steel for piping and internal structural components. While this alloy has excellent general corrosion resistance in high-temperature water, it can be susceptible to intergranular stress-corrosion cracking. The problem results from the grain boundary carbide formation and chromium depletion that accompanies thermal exposure in the range of 600—900 °C. The heat affected zone surrounding a weld, for example, frequently experiences temperatures in that range, leaving a sensitized microstructure. In the late 1960’s and early 1970’s it became apparent that the nominally pure, high-temperature water environment of a BWR’s core recirculation system could promote cracking in sensitized stainless steel piping. Since then nearly 300 pipe cracking incidents have been reported in American reactors (1,2) leading to costly shutdowns for repair, as well as creating some potential safety hazards.

While the use of low-carbon grades of stainless steel and improved welding practice can probably mitigate this problem in future nuclear reactors, existing ones must operate with sensitized weld zones in their piping. Since in-plant weld repair would be prohibitively expensive, research toward preventing reactor pipe cracking has dealt mainly with environmental factors. For several years the Fontana Corrosion Center of the Ohio State University, 1.
under the sponsorship of the Electric Power Research Institute has conducted a research program to determine the effects of various reactor water impurities on stress-corrosion, with the goal of developing water purity standards to prevent future pipe cracking in existing plants.

While previous research has been concerned with inorganic impurities such as sulfate and chloride, this dissertation considers the effects of simple organic acids on high-temperature stress-corrosion. This dissertation presents 1) a review of the present understanding of impurity effects or cracking, along with a discussion of possible sources of organic acid contamination in reactors, 2) a discussion of high temperature solution thermodynamics, 3) a description of the experimental program to determine the effects of organic acids on stress-corrosion cracking in the boiling water reactor environment 4) the results of the experimental program, 5) a detailed discussion and interpretation of the experimental results and their implications for prevention of stress-corrosion, and 6) a summary of the conclusions from this research.
1. LITERATURE SURVEY

A thorough search of the available literature revealed no published reports of stress-corrosion experiments in high temperature organic acid solutions. However, it is appropriate to review both the potential sources of organic acid contamination in nuclear steam systems and the present knowledge of how environmental variables affect stress-corrosion in elevated temperature water.

Organic impurities may enter a nuclear steam system from a variety of sources, including contaminated makeup water (e.g. from condenser leaks), accidental intrusions of oil, detergents, or solvents, and from demineralizer resins (3). Organic acids may form when simple organic compounds are exposed to high temperature oxidizing conditions (4). The core of a boiling water reactor, with temperatures in excess of 250 °C and radiolytically formed oxygen, therefore represents an environment suitable for organic acid synthesis, if the basic organic contaminants are present.

Of the various sources of organic contamination in a reactor, demineralizer resin bed breakup has received the most attention in the literature. These beds consist of several hundred kilograms of fine resin beads, through which low temperature feed water passes on its way to the main reactor vessel. The individual beads are composed of cross-linked polystyrene chains with either acidic or basic groups attached to the benzene rings. The most common acidic
4. The functional group is sulfonate, which attracts cations. The usual basic group is a polymethylamine which removes anions from solution. These structures are illustrated in fig. 1, taken from a review by Pepper and Halverson (5).

Under normal operating conditions resin beads are quite stable. However, they may physically deteriorate, either from age or from temperature excursions in the feed lines (70-90 °C transients), and fine resin particles may then be carried into the reactor core.

Several research groups have considered the effects of high temperature or radiation on the bead material. Kurtz (6) exposed samples of cation and anion resins in separate water filled autoclaves at 288 °C for up to 25 hours. Subsequent analyses of the test water solutions showed considerable splitting of the functional groups from the polystyrene matrix. The cation resin solutions had a very high sulfate content with a low pH, while the anion resin solutions contained both dissolved organic carbon and amine groups. The inorganic sulfate and sulfuric acid contamination released by degradation of cation resins has been the subject of previous stress-corrosion studies. The organic compounds released from anion resins are a potential source of carboxylic acids, whose effects on stress-cracking are the subject of this dissertation. Kurtz also exposed wet resin samples to radiation doses of up to 100 megarads at room temperature. The results of those experiments were similar to the elevated
Figure 1. Chemical Structure of Cation and Anion Resins
temperature exposures. In particular, there was a large release of organic material from the anion resins. Unfortunately Kurtz listed the organic makeup of the test solutions only in terms of total dissolved carbon, providing no more detailed analysis of the compounds present. However this study does show that carbon based compounds, a precursor of carboxylic acid formation, can be released by thermal or radiolytic degradation of demineralizer resins.

Narebska and associates (7) performed similar experiments, exposing an anion resin to radiation doses as high as 2500 megarads. They examined the resultant products by infrared spectroscopy to determine the organic functional groups present. The most significant finding of this study was the development of a strong carbonyl group indication during irradiation. The carbonyl group (C=O) is a component of carboxylic acids, which these authors believe to be a likely product of the resin irradiation.

Narebska believes that the carbonyl group which formed during these experiments is a product of the polystyrene matrix reactions, rather than the methylamine functional groups. However, she reports that the methyl groups are readily freed from the matrix by radiation, thus creating a large component of free organic material. Such free material may also be transformed later to carboxylic acids too. It is clear however from this study that organic acids may be produced by irradiation of demineralizer bed
resins.

Another study, by Fernandez-Prini (8), also considered high temperature effects on deionizer resin. Samples of anion resin were heated in autoclaves for 7 days at 250°C. Infrared analyses of water in contact with the resin confirmed the presence of the C=O group, a sign of organic acid formation. As in Narebska's experiments, the methylamine groups had separated from the polystyrene matrix, liberating a large quantity of organic material.

While none of these studies used both high temperature and irradiation (a very difficult experiment), they do confirm that either heat or radiation can transform demineralizer materials into organic acids, and the core of a reactor satisfies both of those conditions very well.

As mentioned earlier, no reports of stress-corrosion experiments in organic acid solutions at high temperature were found in the literature. However, what is known about the effects of other environmental variables on stress-cracking may shed some light on the possible action of organic acids.

Probably the single most important factor in stress-corrosion of sensitized type 304 stainless steel at elevated temperature is the electrochemical potential. Generally speaking, more anodic potentials promote alloy dissolution at growing cracktips, leading
to more rapid crack propagation. Many authors speak of a critical potential or threshold potential for crack growth. Cragnolino and Agrawal (9) reported a very distinct decrease in failure times of slow-strain rate specimens in 0.01 N Na\textsubscript{2}SO\textsubscript{4} at 250 °C when the potential was maintained above -300 mV (SHE)*. Indig and McIlree (10) conducted experiments in that same solution at 275 °C and reported that below -400 mV, sensitized specimens were immune to stress-corrosion cracking. Poznansky and Duquette (11) also reported a threshold potential effect for cracking in dilute (<100 ppm) sulfate and chloride solutions. They placed the critical potential at -350 mV for their tests in deaerated solutions at 290 °C. Rosengren and Rosberg (12) reported a threshold potential of -300 mV for cracking sensitized slow-strain rate specimens in high purity water at 250 °C. Yonezawa and Tsuruta (13) found no cracking in deaerated 0.025 M Na\textsubscript{2}SO\textsubscript{4} at 300 °C when the specimen potential was more cathodic than -450 mV. In experiments measuring crack growth rates with modified wedge-opening specimens, Chung (14) found that crack propagation ceased below -300 mV in 0.01 M Na\textsubscript{2}SO\textsubscript{4} at 250 °C.

* Throughout this dissertation, the expression "N" refers to normality, or the number of moles of a substance per liter divided by the valance of the dissociated anion. Molarity, or the number of moles per liter, is given as "M" and the weight concentration of a substance in parts per million is designated "ppm". In some reference material concentrations are also expressed in ppb (parts per billion), note 1 ppm = 1000 ppb.
The critical potential for cracking is not a rigid quantity, rather it depends on the alloy and the environment. Macdonald et al (15) report that the critical potential decreases with increasing alloy sensitization and decreases linearly with temperature. The threshold potential also is a strong function of solution chemistry, as will be explained in more detail later in the review.

The potential of a stainless steel surface in aqueous solution can be controlled either potentiostatically, as is often done in laboratory studies, or chemically by a redox system. In the latter case, the potential reaches a steady state at which the rate of cathodic processes (like oxygen reduction) equals that of anodic processes (like alloy dissolution). Dissolved oxygen is probably the most important of chemical species in controlling electrochemical potential in the nuclear environment. Increasing the dissolved oxygen level will increase the stainless steel potential. The exact form of the oxygen-potential relationship follows a sigmoidal or S-shaped curve like the one shown in fig. 2 (from Indig and McIlree (10)). Similar curves have been reported by Kassner (16) and Lee (17). The exact location of the upswing in the curve, however, seems to depend on which researcher measured it, but all agree on the general shape of the curve. Also, for any fixed oxygen level the specimen potential decreases with increasing temperature.
Figure 2. Relationship Between Dissolved Oxygen Content and Type 304 Electrode Potential (274 °C). From reference 10.
Acidity also affects the corrosion potential of stainless steel in aqueous solutions. Protons act as oxidizers, thus with decreasing pH the potential becomes more anodic. An example of pH effects on potential at high temperature is given by Marichev et al (18). These workers measured the potential of type 304 stainless steel in deaerated sulfate solutions at 250°C. The initial solution contained 0.01 M Na₂SO₄ and yielded a potential of -620 mV. As the solution acidity was increased by adding sulfuric acid (at constant total sulfate content) the corrosion potential also increased. At a final concentration of 0.005 M Na₂SO₄ and 0.005 M H₂SO₄ the potential was approximately -380 mV.

While the corrosion potential of stainless steel can be controlled by the oxidizers present in the environment, the critical potential for cracking may be affected by other chemical species present. Among the other species whose effects have been studied are chloride, sulfate, and phosphate. While these substances are quite different chemically from carboxylic acids, their effects may give some indication of the likely workings of the organic compounds.

Data from stress-corrosion cracking experiments in high temperature aqueous solutions are generally of two types. In the first, slow-strain rate specimen failure times are reported as a function of chemical concentration in the water. The dissolved oxygen level is controlled and the specimen potential is that which
results from the solution chemistry. Often researchers neglect to report specimen potentials. In the second type of experiments potential is electronically maintained at a fixed value. For any given series of potentials, the solution chemistry is kept constant and the system is usually deaerated to remove all oxygen. Data are reported in terms of slow-strain rate specimen failure time vs. specimen potential. This type of test is suitable for determining critical potential for cracking in any given test environment. Thus by repeating the potential series at different chemical levels, critical potential can be determined as a function of concentration of the chemical species in question. The problem with this type of test is that the results are difficult to compare with pure water systems. In the absence of a supporting electrolyte, specimen potential is nearly impossible to electronically control. The solution resistance would be so high as to severely overload most practical laboratory power supplies. Potential could be controlled in pure water by varying the dissolved oxygen level, however, such experiments have seldom been performed. If there were a supporting electrolyte known to have no effect on cracking, it could be used for conducting "pure" water experiments under potentiostatic control. Unfortunately no such electrolyte has been recognized and accepted by stress-corrosion researchers.

Hishida and Nakada (19) used the first type of experiment to produce an excellent set of data on the effect of chloride on
stress-cracking of sensitized type 304 stainless steel. Their experiments showed that the failure times of slow-stain rate specimens (\( \dot{\varepsilon} = 5 \times 10^{-4} / \text{min.} \)) in aerated water at 286 C decreased from 16 to 2.5 hours as the chloride content of the solution was raised from 0 to 10 ppm. In these experiments the potential was probably quite high (>0.0 mV) because of the high oxygen content of the test solution. This potential would have been high enough to promote rapid failure in a chloride-free system. It should also be noted that because the chloride was added as NaCl the room temperature pH was probably near neutral.

Duquette and Poznansky (11) conducted the other type of experiment to determine the effects of neutral chloride on cracking. Their studies, using both 1.8 and 100 ppm Cl in deaerated water at 290 C showed approximately the same critical potential for both levels, -200 mV. The failure time at the higher chloride level was much faster. This would imply that chloride has little effect on the critical potential for cracking, but rapidly accelerates crack propagation once that potential has been reached.

The effects of sulfate on stress-corrosion are not so clear, largely because the different types of experiments used by various researchers are difficult to compare. Duquette and Poznansky (11) reported that 100 ppm sulfate (added as sodium salt) has no effect on either the critical potential or crack growth rate in deaerated, 290 C solutions. The problem with their experiments is that they
used 100 ppm chloride as a supporting electrolyte, which may have already created such bad cracking conditions that the sulfate had little additional effect.

Kassner (16), on the other hand, used 0.1 ppm sulfate (sodium salt) and 0.2 ppm oxygen in slow-strain rate tests (1x10^{-6}/sec) at 289 C. His experiments showed a failure time of 50 hours in the sulfate bearing solution, but 160 hours when the sulfate was absent. Experiments with other sulfate salts, including copper, zinc, iron, and chromium sulfates, give similar results.

Andresen and Indig (20) performed a series of stress-corrosion experiments using constant load specimens cycled between 35 and 190 C to simulate nuclear reactor startup cycles. Those experiments, using a fixed dissolved oxygen level of 0.2 ppm, showed that 0.01 M sodium sulfate greatly accelerated failure compared to pure water environments.

Cragnolino and Macdonald (21) reported the results of slow-strain rate experiments using 0.01 M sodium sulfate solutions at 250 C. Under air saturated conditions, failure times were similar for both sulfate bearing and sulfate free solutions. Those experiments contrast with those of Kassner (16) or Andresen and Indig (20) in that a higher oxygen level and hence higher specimen potential was used. Perhaps in the former experiments the potential was so high that the sulfate made little difference, while at lower potentials it could have accelerated
cracking.

While there may be some debate on the effects of neutral sulfate salts on stress-corrosion in reactor systems, sulfuric acid clearly accelerates cracking in high temperature water. Marichev (18) conducted a series of slow-strain rate tests in deaerated sulfate solutions at 250 C with the potential controlled at -200 mV. In those tests the sulfate content was held at a constant 0.01 moles/l, but the cation content was varied from all Na\(^+\) to an equal mixture of Na\(^+\) and H\(^+\) (half salt, half acid). In the totally salt solution, failure time was 36 hours, while in the acidified solution it dropped to 16 hours. Lowering the pH rapidly accelerated cracking.

Ruther and Associates (22) conducted slow-strain rate experiments at 289 C and open circuit potential using 0.2 ppm dissolved oxygen. They found that lowering the room temperature pH from neutral to 4.8 with sulfuric acid additions significantly reduced failure times (from 140 hrs. to 50 hrs.) The increase in acidity clearly accelerated cracking.

As opposed to chloride and sulfate, phosphate additions actually inhibit high temperature stress-corrosion. In experiments performed by Macdonald and associates (15), slow strain rate specimens failed in approximately 72 hours in aerated water at 275 C. When the solution was switched to air saturated 0.002 M Na\(_2\)HPO\(_3\) and 0.008 M H\(_3\)PO\(_4\), the failure time increased to approximately 125
hours. Controlled potential experiments showed the critical potential in the phosphate solution at 250 C to be approximately -100 mV, while the critical value for 0.01 Na₂SO₄ was -400 mV. It should be noted that this phosphate solution has a pH of 6.5 at 250 C, which is approximately that of the sulfate solution. Thus the inhibiting effect of phosphate is not a matter of solution pH.

In summary, sensitized type 304 stainless steel tends to crack in high temperature water when its electrochemical potential is raised above a critical value. Dissolved oxygen is major factor in controlling the potential of stainless steel in aqueous solution. Neutral sulfate probably accelerates stress-corrosion, while sulfuric acid and chloride definitely accelerate it. Neutral phosphate exerts an inhibiting effect on stress-corrosion.
Prior to discussion of the results obtained on this research, some theoretical principles need to be presented. The analysis of the data from the experiments conducted in this research requires the calculation of pH values for the organic acid solutions at both room and elevated temperatures. While room temperature pH can be calculated in a straight forward manner using acid equilibrium constants found in most organic chemistry texts, the elevated temperature constants are not available and must be calculated by the means described in this section.

The equilibrium constant for an acid is related to its standard free energy of dissociation as follows:

$$\Delta G^\circ = -RT \ln K$$  \hspace{1cm} (1)$$

where $K$ is the dissociation constant, $R$ the gas constant, and $T$ the temperature on the Kelvin scale. Thus one needs the elevated temperature energy of dissociation to derive the dissociation constant. That dissociation energy is given by the following equation which includes the changes in entropy and enthalpy that accompany heating to temperature $T_2$ from a reference temperature $T_1$. 

18.
\[ \Delta G = -\Delta C_p - (T - T_1)\Delta S \quad (2) \]

\[ \int_{T_1}^{T_2} 2C_p \, dT + \int_{T_1}^{T_2} \Delta C \, dT \]

To calculate \( \Delta G \) at some elevated temperature using equation (2) the value of \( \Delta C_p \), the difference in heat capacities between the products and reactants of dissociation, is needed. While heat capacity data are readily available for gases and condensed species, they are virtually nonexistent for ions in aqueous solution. Indeed, such heat capacities cannot be directly measured because it is impossible to have just one ionic species in solution. Thus some approach for getting partial ionic heat capacities is required before elevated temperature dissociation constants could be calculated.

In the early 1960's Criss and Cobble of Purdue University (25) conducted some important research aimed at obtaining a theoretical means for calculating high temperature heat capacities of various ions in solution. Since heat capacity and entropy are related by the following formula, \( C_p/T = dS/dt \), they examined how the entropies of dissolved ions vary with temperature, in the hope of finding a simple relationship which could be used to develop heat capacity data. Fortunately there was an adequate amount of entropy data for dissolved ions to allow such a study. Criss and Cobble
observed that for classes of ions (such as simple cations or anions) entropy varies linearly with temperature. That observation they called the "Correspondence Principle", which is mathematically expressed as follows:

\[
S = a + b \frac{S}{T^2} \quad (3)
\]

Where \( a = a + a \frac{T}{T^1} \) and \( b = b + b \frac{T}{T^2} \).

This principle holds for the absolute entropy scale on which the H ion has an entropy of -5 e.u. at 25 C, rather than the conventional scale which assigns the H\(^+\) ion a value of zero. The average heat capacity over a temperature interval is given by

\[
\overline{C_P} = \frac{S - S}{T^2} \quad (4)
\]

\[
= \frac{1}{T^1} \ln \frac{T}{T^2}
\]

Equation 4 can be used to calculate average heat capacities for the various ionic species in the reaction yielding \( C_P \), which can then be used in equation 2 to calculate the free energy of dissociation at elevated temperature and, hence, the dissociation constant.

The observed values of \( a \) and \( b \) for use along with room temperature entropy data in equation 3 are given in table 1, which assumes the low temperature to be 25 C.
**Table 1. Summary of Entropy Constants for Equation 3**

<table>
<thead>
<tr>
<th>T°C</th>
<th>Simple Cations</th>
<th>Simple Anions</th>
<th>Oxyanions</th>
<th>Acid Oxyanions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>1.000</td>
<td>0</td>
<td>1.000</td>
</tr>
<tr>
<td>60</td>
<td>3.9</td>
<td>.955</td>
<td>5.1</td>
<td>.969</td>
</tr>
<tr>
<td>100</td>
<td>10.3</td>
<td>.876</td>
<td>-13.0</td>
<td>1.000</td>
</tr>
<tr>
<td>150</td>
<td>16.2</td>
<td>.792</td>
<td>-21.3</td>
<td>.989</td>
</tr>
<tr>
<td>200</td>
<td>23.3</td>
<td>.711</td>
<td>-30.2</td>
<td>.981</td>
</tr>
<tr>
<td>275</td>
<td>32.9</td>
<td>.583</td>
<td>-43.1</td>
<td>.980</td>
</tr>
</tbody>
</table>
Probably the most significant finding of Criss and Cobble's research is that the same parameters apply for broad classes of ions. Thus one need not develop separate parameters for each individual species. Such similar behavior within a class of ions would not be expected. In fact, even Criss and Cobble stated

"It would be surprising to find that the correspondence principle could be accurately applied to complex ions since these species have internal degrees of freedom and their internal contributions to the entropies and heat capacities would be expected to vary from ion to ion. However good correlations exist..." (25)

The power of this principle then lies in the fact that the researcher needs only the room temperature entropy of an ion, from one of these broad classes, to calculate its heat capacity at elevated temperatures. Room temperature entropy data are available for a number of ions and are compiled into a report by the United States Bureau of Mines (26). Even if the room temperature entropy of some species were not available in the literature, it might be estimated using empirical techniques given by either Connick and Powell (27) or Couture and Laidler (28).

An example of the calculations using these techniques follows for oxalic acid at 275 C.

\[
\text{Room Temp. } K = 5.40 \times 10^{-2} \text{ (First Dissociation)} \\
\Delta G \text{ at } 298 \text{ K} = 1722 \text{ cal/mole}
\]
Table 2. Necessary Thermodynamic Data (Values in e.u.)

<table>
<thead>
<tr>
<th></th>
<th>S (298 K)</th>
<th>S (548 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>proton (H⁺)</td>
<td>-5.0</td>
<td>18.4</td>
</tr>
<tr>
<td>anion (HC₂O⁻)</td>
<td>36.7</td>
<td>38.9</td>
</tr>
<tr>
<td>undiss. acid (H₂C₂O₄)</td>
<td>35.5</td>
<td>71.9</td>
</tr>
</tbody>
</table>

Room temperature values (298 K) are taken from the Bureau of Mines report. Elevated temperature entropy values for the anion and proton are calculated by Criss and Cobble's technique. The high temperature value for the undissociated acid comes from tables of Barner and Scheuerman (29). Using equation 4 the following average heat capacity values are derived for the interval 298 K to 548 K.

Table 3. Heat Capacities For Oxalic Acid Dissolution

<table>
<thead>
<tr>
<th></th>
<th>C cal/°mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>proton</td>
<td>38.5</td>
</tr>
<tr>
<td>anion</td>
<td>3.6</td>
</tr>
<tr>
<td>acid</td>
<td>59.7</td>
</tr>
</tbody>
</table>

\[ \Delta C = -17.6 \text{ cal/°mole} \]

Substituting the room temperature values of \( \Delta G \) and \( \Delta S \), as
well as the calculated $\Delta C_p$ into equation 2 yields a $\Delta G$ for
dissociation at 548 K (275 C) of 4150 cal/mole. From equation 1
it is seen that this value of free energy corresponds to a
dissociation constant of $2.18 \times 10^{-2}$ at the elevated temperature.
For a concentration of $4.35 \times 10^{-4}$ M (equimolar to 20 ppm formic
acid) the pH would be 3.4 at 548 K. Tables 4 and 5 give the
dissociation constants for the other acids and the pH values of the
experimental solutions at room and elevated temperatures.

The Criss and Cobble technique provides a powerful tool for
elevated temperature thermodynamics and solution chemistry.
However, it has some practical limitations. Criss and Cobble
themselves, warn that one should exercise caution in extrapolating
their entropy constants above 200 C because the linear relationship
may not be valid at higher temperatures. Those authors have
contemplated further research to develop the entropy-temperature
relationship above 200 C, but they have yet to publish anything on
that subject.

To test the validity of the correspondence principle
calculated values for an organic acid's dissociation constant at
high temperatures should be compared against experimentally
observed values. Unfortunately high-temperature dissociation
constant data for organic acids are virtually nonexistent. A
review of the literature revealed only one such study from a
Western source. Lown and Thirsk (30) measured the pK values of
### Table 4. Organic Acid Dissociation Constants

<table>
<thead>
<tr>
<th></th>
<th>25 C</th>
<th>275 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOOH</td>
<td>1.78 x 10^{-4}</td>
<td>1.66 x 10^{-5}</td>
</tr>
<tr>
<td>CH_3COOH</td>
<td>1.75 x 10^{-5}</td>
<td>5.01 x 10^{-7}</td>
</tr>
<tr>
<td>COOH</td>
<td>5.40 x 10^{-2}</td>
<td>2.18 x 10^{-2}</td>
</tr>
</tbody>
</table>
Table 5. PH Values for Organic Acid Solutions

<table>
<thead>
<tr>
<th></th>
<th>25 C</th>
<th>275 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOOH (20 ppm)</td>
<td>3.4</td>
<td>4.1</td>
</tr>
<tr>
<td>CH₃COOH (26 ppm)</td>
<td>4.1</td>
<td>4.8</td>
</tr>
<tr>
<td>C₂H₂O₄ (38 ppm)</td>
<td>3.4</td>
<td>3.4</td>
</tr>
<tr>
<td>CH₃COOH (104 ppm)</td>
<td>3.8</td>
<td>4.5</td>
</tr>
</tbody>
</table>
acetic acid up to 375 C. Their values, as well as calculations conducted in the present study using the Criss and Cobble approach appear in table 6.

As the table shows there is reasonably good agreement between the calculated and observed values between 100 C and 300 C (the range of interest in this program). Above these temperatures the Criss and Cobble approach is probably invalid.

Unfortunately there are no reliable experimental observations for formic or oxalic acids above 200 C. Maksimova and Yushkevich (31) reported dissociation constants for several acids, including the three organic acids used in the present investigation, from 20 to 300 C. Their values disagree with the calculated and observed values for acetic acid given in table 8, and also they do not agree with the established room temperature values. Therefore that work should be disregarded for purposes of validating high-temperature acidity calculations.

In the absence of any more experimentally observed high-temperature dissociation constant data, the approximation techniques described in this appendix must suffice. However the available data do indicate that these calculations are reasonably accurate in the temperature range under consideration.

The Criss and Cobble techniques can also be used to calculate the overall free energy changes and, hence, equilibrium constants
Table 6. High-Temperature pK Values for Acetic Acid

<table>
<thead>
<tr>
<th>Temperature C</th>
<th>Calculated pK</th>
<th>Observed pK</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>4.99</td>
<td>4.94</td>
</tr>
<tr>
<td>150</td>
<td>5.34</td>
<td>5.18</td>
</tr>
<tr>
<td>200</td>
<td>5.84</td>
<td>5.48</td>
</tr>
<tr>
<td>250</td>
<td>6.20</td>
<td>5.86</td>
</tr>
<tr>
<td>275</td>
<td>6.36</td>
<td>6.22</td>
</tr>
<tr>
<td>300</td>
<td>6.46</td>
<td>6.59</td>
</tr>
</tbody>
</table>
for the oxidation and thermal decomposition of the organic acids. Table 7 presents those values for the aqueous oxidation reactions at 275°C (based on input data from the same sources cited for the pH calculations). As the table shows, aqueous phase oxidation of all three acids is thermodynamically very favorable. Kinetic factors, however, limit the actual degree of acid consumption during each experiment.

In addition to oxidation, thermal decomposition of the acids must also be considered. Using the same thermodynamics approaches, the free energies and equilibrium constants for acid decomposition were calculated. Those data appear in table 8.
Table 7. Free Energies of Organic Acid Combustion
(Aqueous Phase)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔG (Kcal/mole)</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOOH + 1/2 O → CO</td>
<td>-61.2</td>
<td>2.6 \times 10^2</td>
</tr>
<tr>
<td>CH_3COOH + 2O →</td>
<td>-187.6</td>
<td>6.7 \times 10^3</td>
</tr>
<tr>
<td>2CO + 2H_2O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_4H_6 + 1/2 O →</td>
<td>-86.6</td>
<td>3.5 \times 10^2</td>
</tr>
<tr>
<td>2CO + H_2O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Table 8. Decomposition of Organic Acids in High Temperature Aqueous Solutions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G$ (kcal./mole)</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>275 $^\circ$C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCOOH $\rightarrow$ CO + H</td>
<td>-13.6</td>
<td>$2.7 \times 10^5$</td>
</tr>
<tr>
<td>CH$_3$COOH + 2H$_2$O $\rightarrow$</td>
<td>3.5</td>
<td>$4.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>2CO + 4H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$O + H</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3. EXPERIMENTAL PROCEDURES

3.1 Stress-Corrosion Cracking Test Procedures

The principal experimental procedure used in this research program was the slow-strain rate test (SSR). This procedure employs a tensile specimen which is continuously elongated in both an inert and a test environment at some fixed low rate. The specimen will fail in an inert environment by ductile rupture, whereas exposure to a corrosive environment often promotes more rapid failure, which is indicative of stress-corrosion. Thus variations in time to failure is one of the major methods for determining susceptibility to stress-corrosion cracking. In addition, the appearance of the fracture face and the degree of secondary cracking indicate the failure mode.

The test specimens are illustrated in fig 3, and were machined from 1/4 inch (6.25 mm) diameter AISI type 304 stainless steel. The composition and original mechanical properties of this heat of steel are given in tables 9 and 10. Specimens were solution annealed for 1/2 hour at 1050°C and then water quenched, after which they were then sensitized for 24 hours at 650°C. All heat treatments were conducted in an argon atmosphere furnace to avoid excessive surface oxidation. Prior to use the specimens were polished to a 600 grit finish with silicon carbide paper and degreased in acetone.

Figure 4 shows a specimen loaded in the autoclave vessel. The
Table 9. Composition of AISI Type 304 Stainless Steel Used in Study  
(Weight Percentages)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.064</td>
<td>18.22</td>
<td>9.58</td>
<td>1.04</td>
<td>0.025</td>
<td>0.023</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Mo</th>
<th>Cu</th>
<th>Co</th>
<th>N</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.330</td>
<td>0.440</td>
<td>0.14</td>
<td>0.042</td>
<td>0.420</td>
</tr>
</tbody>
</table>

Table 10. Mechanical Properties of the Alloy

<table>
<thead>
<tr>
<th></th>
<th>Tensile KSI.</th>
<th>Yield 0.2% KSI.</th>
<th>Reduction in Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>114.0</td>
<td>82.0</td>
<td>74.0</td>
</tr>
<tr>
<td>Elongation</td>
<td>46.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Dimensions of the Tensile Specimen

Figure 3. Test Specimen For Slow Strain Rate Experiments
bottom of the specimen was secured by a hold-down nut which, in turn, was held by the specimen yoke. An alumina washer around the specimen insulated the hold-down nut from the autoclave. The alumina washer was selected after teflon insulation failed during tests, causing a short circuit between the specimen and the vessel. The hold-down nut was wrapped with teflon, along with all of the specimen but the gage length, to isolate it from the solution. In this manner the effects of all but the gage length region on specimen potential were eliminated. The specimen passed through the vessel by means of a teflon gland in a Conax fitting, which allowed movement but prevented pressure loss.

A variable speed electric motor and a series of reducing gears provided the specimen loading and slow elongation. The test strain rate, $1 \times 10^{-6}$/sec, was calibrated using a mechanical dial gage attached to the crosshead movement. The load on a specimen was determined with a load cell, having a calibrated output of 1 mV per 100 lbs loading. The initial specimen load was approximately 100 lbs, which produced a specimen gage section stress of 12,750 psi (well below the 0.2% offset yield criteria).

The specimens were exposed at their steady-state corrosion potentials. No electronic potential control was used.

3.2 Water Chemistry and Control Systems

The high temperature water environment needed for these tests
Figure 4. Specimen in Autoclave
was maintained in a pressurized, recirculating autoclave system shown schematically in fig. 5. Conditioned water passed from a storage reservoir to a pump, where it is pressurized, and passed through the heat exchanger (countercurrent to return flow) prior to injection into the vessel. From the vessel the water returned through the regenerative heat exchanger, followed by a second water cooled heat exchanger and a depressurizing valve, to either the original reservoir or to a drainpipe. The system could operate either in a recirculating or once-through mode. In the recirculating mode a 60 liter reservoir was used. In the once-through mode the original reservoir was supplemented with a 90 liter tank.

The test temperature was 275°C and test pressure was 1200 psi, which is considerably higher than the saturated steam pressure; therefore no steam phase forms in the system. Fluid flow was 1 liter/hr. The autoclave was enclosed in a heating jacket to maintain a constant test temperature, and the heating system was controlled by two thermostats wired in series. The first was connected to a thermocouple in the autoclave to maintain the solution temperature. The second prevented overheating of the heating jacket.

The dissolved oxygen content in the solution was adjusted by bubbling various mixes of oxygen and nitrogen through the reservoir tanks. The gas ratios were controlled by a flow metering system. In some cases cylinders of premixed oxygen and nitrogen were used, rather than blending from separate cylinders in the laboratory.
Figure 5. Schematic Diagram of Recirculating Loop and Autoclave System
Precautions were taken to avoid trapping air in the autoclave during the original filling.

Dissolved oxygen concentrations were measured with a Leeds and Northrup model 7931 dissolved oxygen monitor. This instrument was placed either in the reservoir for input oxygen concentration or in the depressurized, low temperature part of the return line for exit concentrations. Actual in-vessel measurements were not possible because of the elevated temperature. The monitor's minimum sensitivity was approximately 0.005 ppm. The range of dissolved oxygen measurements was verified using the CHEMet colorimetric system.

Solution acidity was initially measured in both the tank and return line using a bench-top pH meter. In later tests the system was fitted with permanent pH electrodes in both stations, for continuous measurements. Electrode potentials from pH probes (which were converted to pH values) were measured using an ultra-high impedance amplifier. These measurements were calibrated using standard pH reference solutions. As with dissolved oxygen measurements, pH readings were necessarily taken in nonpressurized room temperature parts of the system. Techniques for converting room temperature pH values to those at elevated temperature have been described in a previous section.

All data measurements including load cell, pH probe, dissolved oxygen, and specimen potentials were recorded with an Esterline Angus
model PD 2064 data acquisition system. That system provided a paper printout of those readings at regular programmed intervals.

3.3 Electrochemical Measurements

Electrode potential measurements were made using a pressure balanced Ag/AgCl reference electrode described by Macdonald (23). That electrode, shown in fig. 6, consists of a silver wire, coated with a silver chloride scale, in a tube filled with 0.1 N AgCl solution. The silver wire end of the electrode is cooled to room temperature by a water jacket, while the other end enters the autoclave. A finely porous zirconia plug on the autoclave end of the electrode allows electrolytic conductivity between the specimen and silver wire, while preventing the chloride solution from escaping. Macdonald's article derives the conversion factors needed to relate the potential of this electrode to the standard hydrogen electrode scale at the test temperature. The conversion included both the change in hydrogen electrode potential with temperature, and the liquid junction potential between hot and cold ends of the electrode. At 275 C the room temperature AgCl electrode value can be converted to the SHE value by subtracting 20 mV. Non-stressed platinum and type 304 stainless steel electrode potential measurements were also included in the later tests of the program. Insulated lead-in wires, sealed by a special teflon fitting in a Conax joint, connected these
Figure 6. Reference Electrode Assembly
electrodes to an external potentiometer.

To aid in interpreting the electrochemical processes which occur in the high temperature acidic solutions, cathodic polarization tests were conducted. In those experiments a cylindrical specimen of type 304 stainless steel (surface area = 3.5 sq.cm.) heat-treated and finished the same as the slow-strain rate specimens was used. The specimen was connected to a Wenking potentiostat by an insulated lead-in wire, while the autoclave vessel served as the counter electrode. Potentials were measured against the Ag/AgCl reference electrode. The potential was increased in the negative direction at a rate of 25 mV every 2 minutes. The conductivity of acid-free solutions was augmented with an addition of 0.01 N Na SO₂.

Although cathodic polarization curves can be useful in determining the effects of both oxygen and the organic acids on the electrode kinetics of the system, in dilute solutions they must be analyzed carefully to eliminate the various spurious components of specimen potential. To achieve this the curves were analyzed in the following manner. As described in the classic treatise by Stern and Geary (32), the overpotential measured in a cathodic polarization test is the sum of three components. The first is the activation potential, which is mathematically described as follows:

\[ \eta = \beta \log \frac{i_f + i_a}{i_o} \]  

(5)

where \( \eta \) is the overpotential, \( \beta \) the Tafel slope, \( i_o \) the exchange current, and \( i_f \) and \( i_a \), the cathodic and anodic currents. Except
at potentials close to the corrosion potential, the cathodic current term greatly exceeds the anodic component, and may be treated as the sole current in equation (5). As the equation shows, under activation control a plot of overpotential vs. logarithm of current would be a straight line except at very small overpotentials.

The second component of overpotential is the solution resistance term. As ionic current flows between the counter and working electrodes of a cell, it is accompanied by a voltage drop. Since there must be some finite distance between the reference and working electrodes, the voltage drop across that gap will be added to the activation component of overpotential. That resistance component is given as:

\[ n = IR \]  \hspace{1cm} (6)

where \( I \) is the total specimen current and \( R \) the effective cell resistance between the reference and working electrodes. In high purity water or dilute acid solutions that resistance term can become significant because of low solution conductivity. In acid-free experiments an addition of 0.01 N \( \text{Na}_2\text{SO}_4 \) raised the solution conductivity sufficiently to make the IR drop nearly negligible. However, to avoid the possibility of any complicating chemical interactions, no sulfate was added to the organic acid solutions. Thus solution resistance was high and the resistance component of overpotential was significant in the acid solutions.

The magnitude of cell resistance was determined using a current
interrupt technique. In this procedure the specimen was polarized to some moderate cathodic overpotential and the current recorded at steady-state. The polarization was then interrupted and the resulting decay in potential was recorded (in this case on a strip-chart recorder). As shown in fig. 7, the specimen potential undergoes an instantaneous drop, corresponding to the IR loss, followed by a slower decrease as it returns to its corrosion potential. Since the current was recorded immediately before disconnecting the polarization, the effective resistance of the system can be calculated from the instantaneous potential drop using equation (6).

The third component of overpotential is that of concentration polarization, which results from limitations in diffusion of the reduced species to the specimen surface. This term is given by:

\[
\eta = -\frac{2.3RT}{F} \log \left( 1 - \frac{I}{I_L} \right) \quad (7)
\]

where \( I_L \) is the limiting current at high overpotential. Assuming oxygen to be the reduced species (\( n=4 \)) and temperature to be 275 C (548 K) the prelogarithmic term is calculated as 27 mV. Thus a cathodic current of 90% of the limiting value produces a concentration potential component of only 27 mV. Increasing the current to 99% of the limiting value raises the concentration polarization term to 54 mV. Thus the concentration polarization effect is only significant at high current densities and hence, at high overpotentials.
Figure 7. Graph of Potential During Polarization Interrupt Test
The effect of these three components is additive, resulting in the following expression for the indicated overpotential:

\[ \eta = \theta \log \frac{i_x + i_r}{i} + i \chi R + \frac{RT}{nF} 2.3 \log \left( 1 - \frac{I}{I_L} \right) \]  

When comparing polarization curves made under different conditions in this research the effects of the different components of overpotential was considered, particularly when the solution conductivities varied greatly. In the Results section these corrections were applied to the analysis of raw data from several cathodic polarization experiments, thus facilitating a proper comparison.
4. EXPERIMENTAL RESULTS

4.1 Acid-Free Slow-Strain Rate Experiments

These experiments were conducted in high purity water which had been both distilled and deionized. The typical conductivity value was < 0.8 micromho. Originally three dissolved oxygen levels were selected: 8 ppm, which results from air saturation; < 0.005 ppm, which results from nitrogen sparging, and 0.2 ppm, which is typical of the boiling water reactor operating conditions. Return-line measurements showed 0.04-0.07 ppm O₂, when the input level was 0.2 ppm, indicating considerable oxygen consumption in the stainless steel autoclave and recirculating loop system. Thus an additional oxygen level of 0.6 ppm was chosen, because it yielded a return line level of approximately 0.2 ppm. When the input oxygen level was 8 ppm the return line concentration was essentially unchanged. Oxygen consumption appears to be a problem only in the low concentration range of input oxygen.

Data for acid-free experiments appear in table 11. Tests 2 and 3 with 8 ppm O₂, may be questionable because the hold-down nut which gripped the specimen (fig. 5) short circuited to the yoke at sometime during the tests. Resistance measurements after these tests showed contact between the vessel and the specimens. In the rest of the experiments the teflon was replaced with a ceramic
washer, which assured electrical isolation of the specimen. Test 7, a valid test, using the washer for insulation, had approximately the same failure time as 2 and 3 (73 hours). The deaerated environment produced the longest failure time of 115 hours, which is used as a standard for comparison with the other experiments (on all tables the term in parenthesis is the ratio of specimen failure time to that in pure deaerated water). Failure times at 0.2 ppm were approximately the same as at 8 ppm. While at 0.6 ppm failure occurred much more rapidly. It appears that failure times decrease as the input oxygen level is raised from 0 to 0.6 ppm, but then increase as it is further raised to 8 ppm.

Electrode potential data show a general trend of increasing potential with increasing oxygen level as discussed in the literature review. The potentials at intermediated oxygen levels (0.2-0.6 ppm) show some scatter. This is the region in which the S-curve of potential vs. oxygen content rises sharply and the exact relationship between the two is not well defined. Kassner (16) also reported a wide scatter of potentials in this region. Nevertheless, the general form of these data show that increasing oxygen levels produce more anodic potentials.
Table 11. Acid-Free Environments

<table>
<thead>
<tr>
<th>TEST</th>
<th>INPUT 0 PPM</th>
<th>POTENTIAL mV (SHE)</th>
<th>FAILURE TIME Hrs.</th>
<th>NOTES</th>
<th>IGSCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>8.0</td>
<td>30</td>
<td>76.5 (.66)</td>
<td>1. Y</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>8.0</td>
<td>10</td>
<td>73.0 (.63)</td>
<td>1. Y</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>8.0</td>
<td>40</td>
<td>72.5 (.63)</td>
<td>2. Y</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.20</td>
<td>-95</td>
<td>79.0 (.69)</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.20</td>
<td>-105</td>
<td>72.0 (.63)</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>&lt;.010</td>
<td>-580</td>
<td>115.0 (1.00)</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>0.50</td>
<td>-80</td>
<td>58.0 (.50)</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>0.60</td>
<td>-155</td>
<td>55.0 (.48)</td>
<td>Y</td>
<td></td>
</tr>
</tbody>
</table>

Note 1. Probable short circuit to vessel

Note 2. First use of ceramic insulating washer
4.2 Formic Acid Experiments

Slow-strain rate experiments were conducted with 20 weight ppm formic acid solutions (4.35 X 10^{-4} M). This concentration typically yielded a room temperature pH of 3.4 and conductivity of 70 micromhos. While such a concentration is higher than would normally be expected to occur in a reactor (such high conductivity would necessitate a shutdown), it was chosen to accelerate the effect of the acid for the preliminary investigation. The experimental data are given in table 12.

At an 8 ppm input dissolved oxygen level, formic acid addition had no effect when compared with acid-free tests. When the dissolved oxygen level was lowered to either 0.2 or 0.6 ppm the failure time increases dramatically, while specimen potentials shifted by nearly 400 mV in the negative direction. On the other hand, under deaerated conditions, the acid accelerated failure when compared with acid-free tests and also slightly raised the potential.

In experiments 11 and 14 using the recirculating mode system configuration, the specimen potentials began to rise after approximately 70 hours, going from -470 to -170 mV during the next 30 to 40 hours. During that same time period the reservoir pH rose considerably, from 3.5 to 5.1, since the pH in the return line from
the autoclave was always somewhat higher than the input. Thus solution chemistry was not constant during those experiments. The question arose as to whether the rise in specimen potential resulted from the rise in solution pH or from some other process, like specimen oxidation. To answer this question the autoclave was fitted with larger solution tanks and run in a once-through, non-recirculating mode. In this manner the input chemistry was kept constant, and in test #24, with 0.2 ppm \( \text{O}_2 \) the specimen potential remained at a low -520 mV. The input pH was 3.4 and the output pH was 4.0, indicating acid consumption in the autoclave. However, in the once-through mode the acid consumption could not affect the subsequent input pH. From experiment 24 it would appear that the rise in specimen potential seen in tests 11 and 14 was definitely related to solution acidity. When the input oxygen concentration was raised to 0.6 ppm (exp. 28) the results were much the same as in 24. The specimen potential remained at a low value of -470 mV (somewhat higher than the -520 of exp.24) throughout the test, and the exit-line pH was 4.0, the same as in 24. Again, keeping constant input chemistry produced a constant specimen potential.

In all of the 0.2 and 0.6 ppm \( \text{O}_2 \) experiments with formic acid the return line oxygen level was less than 0.005 ppm. In acid-free experiments those input \( \text{O}_2 \) levels yielded outputs of 0.05 and 0.20 ppm respectively. Therefore oxygen is clearly being consumed in acid-free tests as well as in formic acid tests, however the oxygen consumption was nearly complete in the acid bearing environments.
The interactions between formic acid, oxygen, and specimen potential, as well as their effects on cracking, will be treated further in the discussion section.
Table 12. Formic Acid Environments

<table>
<thead>
<tr>
<th>TEST</th>
<th>INPUT O₂ PPM</th>
<th>POTENTIAL mV (SHE)</th>
<th>FAILURE TIME Hrs</th>
<th>NOTES</th>
<th>IGSCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>8.0</td>
<td>55</td>
<td>71.0 (.62)</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.2</td>
<td>-460 → -160</td>
<td>119.0 (1.03)</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0.2</td>
<td>-470 → -170</td>
<td>101.0 (.88)</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>&lt; .010</td>
<td>-480</td>
<td>93.0 (.81)</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>&lt; .010</td>
<td>-470</td>
<td>91.0 (.79)</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>0.2</td>
<td>-495</td>
<td>107.0 (.93)</td>
<td>1. N</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>0.6</td>
<td>-480</td>
<td>105.0 (.91)</td>
<td>1. N</td>
<td></td>
</tr>
</tbody>
</table>

Note 1. Once-through system
4.3 Acetic Acid Experiments

Acetic acid experiments were conducted with a concentration of 26 ppm (equimolar to that used in formic acid tests) which yields a room temperature pH of 4.0 and conductivity of approximately 30 micromhos. The results of those experiments appear in table 13.

At an input O level of 8 ppm the acetic acid addition may have slightly accelerated cracking and increased electrode potential somewhat compared to an acid-free environment, however the changes were quite small. At 0.6 ppm O there appeared to be no effect of acid on either the specimen potential or the cracking time. In a deaerated environment acetic acid resulted in a slight rise in electrode potential and no significant change in the cracking time.

The greatest effect of acetic acid occurred when the input dissolved oxygen content was 0.2 ppm. The failure time decreased to less than 40 hours, compared with approximately 73 hours in the acid-free tests. No conclusive statement can be made about potential, because test 15 had an average value of -90 mV while the potential in test 16 was -65 mV. The rapid cracking in these tests is significant because it exceeds not only that of acid-free solutions at the same oxygen level, but also that of air-saturated solutions with much more anodic potentials. The possible mechanisms of these effects are considered in the Discussion section.
### Table 13. Acetic Acid Environments

<table>
<thead>
<tr>
<th>TEST</th>
<th>INPUT O₂ PPM</th>
<th>POTENTIAL mV (SHE)</th>
<th>FAILURE TIME Hrs.</th>
<th>NOTES</th>
<th>IGSCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>8.0</td>
<td>145</td>
<td>66.0 (.59)</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.2</td>
<td>-90</td>
<td>33.0 (.29)</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>0.2</td>
<td>-55</td>
<td>39.0 (.34)</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>&lt;.010</td>
<td>-475</td>
<td>111.0 (.97)</td>
<td></td>
<td>N</td>
</tr>
<tr>
<td>29</td>
<td>0.6</td>
<td>-80</td>
<td>58.0 (.50)</td>
<td>1. Y</td>
<td></td>
</tr>
</tbody>
</table>

**Note 1.** Once-through system
4.4 Oxalic Acid Experiments

Oxalic acid experiments were conducted at a concentration of 38 ppm (54 ppm of the dihydrated reagent), equimolar to the other acids. Results of those experiments are given in table 14.

Under deaerated conditions the failure time was the same as that of acid-free solutions. At both 0.2 and 0.6 ppm input oxygen, oxalic acid had an inhibiting effect on stress-corrosion, similar to that observed with formic acid, leading to long failure times. Similar to formic acid, the specimen potentials were depressed considerably at the low oxygen levels, and return-line oxygen levels were virtually zero in experiments at 0.2 and 0.6 ppm input oxygen.

When an air saturated solution was used, oxalic acid accelerated cracking, somewhat, compared to acid-free solutions (60 hours failure time vs. approximately 72 hours for acid-free). The return-line $O_2$ level was 4 ppm during the air saturated experiments, indicating considerable oxygen consumption. In all of the oxalic acid tests the return-line pH was considerably higher than the input, a sign of acid oxidation and/or decomposition at the higher temperatures.
Table 14. Oxalic Acid Environments

<table>
<thead>
<tr>
<th>TEST</th>
<th>INPUT O₂</th>
<th>POTENTIAL</th>
<th>FAILURE TIME</th>
<th>NOTES</th>
<th>IGSCC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PPM</td>
<td>mV (SHE)</td>
<td>Hrs.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>0.2</td>
<td>-515</td>
<td>92.0 (.80)</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>0.2</td>
<td>-530</td>
<td>106.0 (.94)</td>
<td>1. N</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>&lt;.010</td>
<td>-540</td>
<td>117.0 (1.02)</td>
<td>1. N</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>0.60</td>
<td>-520</td>
<td>109.0 (.95)</td>
<td>1. N</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>8.0</td>
<td>25</td>
<td>60.0 (.52)</td>
<td>1. Y</td>
<td></td>
</tr>
</tbody>
</table>

Note 1. Once-through system
4.5 Acid Addition Experiments

The slow-strain rate experiments showed that at low oxygen levels (0.2 and 0.6 ppm) formic and oxalic acids produced significant cathodic shifts in specimen potential, while all three acids reduced the return-line oxygen content. To investigate further the effects of these acids on specimen passivation and electrode potential, the following experiment was conducted: A type 304 stainless steel specimen was exposed for 48 hours in air-saturated water at 275°C to build a passive surface film. The solution was quickly deaerated to 200 ppb $O_2$ and maintained at the level for 48 more hours. At this point an addition of one of the acids ($4.35 \times 10^{-4}$ molar) was made to the reservoir and the resulting potentials of the stainless steel and platinum electrodes and the return-line oxygen concentration were recorded. The time delay between the autoclave and the dissolved oxygen monitor was only 3 minutes, so the data are approximately real-time.

When either formic or oxalic acids were added the specimen potentials fell dramatically, accompanied by a decrease in return-line oxygen content, as shown graphically in figure 8 (results for both acids are similar). These results are compatible with oxygen scavenging and depletion by reaction with the acid. Similar results were reported by Cagnolino (21) for experiments in
which hydrogen (a known oxygen scavenger) was injected into a stable, oxygen bearing system. In both groups of experiments, the platinum potential fell much faster than the stainless steel potential, which would be expected because the platinum potential is in constant equilibrium with the environment, whereas depassivation of the stainless steel electrode takes some time.

When acetic acid was added to the system, the stainless steel potential rose briefly then dropped, as shown in fig. 8. Overall the potential change was not great and remained near the range seen in slow-strain rate experiments at that acid and oxygen level. The return-line oxygen level dropped considerably following acetic acid addition.

From these experiments it appears that formic and oxalic acids, at these concentrations, have a strong depassivating effect on stainless steel, whereas acetic acid has little or no effect.

4.6 Cathodic Polarization Experiments

Stress-corrosion in high temperature aqueous solutions is critically dependent on specimen electrode potential. The potential results from the balancing of surface oxidation and reduction processes (of which reduction of dissolved oxygen is one of the most important). To better understand these surface reactions, cathodic polarization experiments were conducted on type
Figure 8. Data From Acid-Addition Experiments
304 stainless steel in various solutions at 275 C. In all cases
the control was potentiostatic, using 25 mV steps at approximately
2 minute intervals.

Figure 9 shows the cathodic polarization curves for a
deraerated 20 ppm formic acid solution, the same solution with 0.6
ppm O_2, and acid-free water with 0.6 ppm O_2 (in acid-free
polarization curves, 0.001 N Na_2SO_4 was added to provide sufficient
conductivity for testing). The two formic acid curves are
virtually identical, with a low corrosion potential near that of
the equilibrium potential for this pH. The limiting currents and
intermediate behavior of these two curves are also quite similar.
Thus it appears that 0.6 ppm of dissolved oxygen has no effect on
the cathodic electrode reactions of type 304 stainless steel in 20
ppm formic acid solutions. In comparison, the acid-free solution
with 0.6 ppm O_2 shows a much higher potential range, for any
cathodic current. The results of these experiments are consistent
with the observed rapid deoxidation caused by formic acid
consumption. Such effective oxygen consumption makes the curve for
the O_2 bearing solution similar to the deaerated one. In a sense,
both solutions are oxygen-free because formic acid oxidation
eliminates most of the oxygen in the 0.6 ppm input oxygen
environment.

Figure 10 shows the cathodic polarization curve for a solution
with 36 ppm oxalic acid and 600 ppb input oxygen. This curve is
Figure 9. Cathodic Polarization Curves for Formic Acid Solutions
Figure 10. Cathodic Polarization Curve for Oxalic Acid Solution
very similar to the formic acid curves. Again, the oxygen is probably consumed by the acid so rapidly that it plays only a very small role, if any, in the electrode processes.

Figure 11 shows the raw curves for acid-free, 26 ppm acetic acid, and 104 ppm acetic acid solutions. A comparison of these curves is somewhat more complicated than in the case of formic or oxalic acids. The acid-free and 26 ppm acid curves have nearly the same corrosion potential while the acid curve has a lower current for any given overpotential. By themselves these two curves would imply that 26 ppm of acetic acid significantly reduces the amount of oxygen available for reduction on the specimen surface. However, when the two curves are corrected for the voltage drop resulting from the solution resistance (as described in the Experimental Procedure section) the two curves nearly superimpose. Fig. 12 shows those curves corrected for the IR loss component of the corrosion cell. Also shown is the 104 ppm acetic acid curve, adjusted for that same correction. The higher acid curve shows a much lower corrosion potential than the other two, and in the uncorrected form resembles that of formic or oxalic acid, in which oxygen plays essentially no role. Thus the increase in acetic acid to 104 ppm appears to have effectively scavenged the dissolved oxygen from the system, while 26 ppm of acid left enough oxygen to polarize the specimen nearly the same as an acid-free solution.

(The values of cell resistance measured by the voltage interrupt technique were as follows: for acid-free sulfate solution, 165
Figure 11. Cathodic Polarization Curves for Acetic Acid Solutions
Figure 12. Cathodic Polarization Curves for Acetic Acid Solutions, Corrected for Cell Resistance
ohms, for 26 ppm acetic acid solution, 4000 ohms, and for the 104 ppm acetic acid solution, 1750 ohms).

The effects of reduced oxygen content on specimen potential can be explained in terms of mixed potential theory. The specimen steady state mixed potential in a freely corroding system must be such that the rate of cathodic processes be equal to that of the anodic processes e.g. a potential where the oxidation and reduction rates vs. potential intersect. This concept is illustrated in fig. 13 based on research by Lee (17). The plot includes the anodic dissolution curve for type 304 stainless steel at 250 °C, which shows a region of passive behavior, and the cathodic reduction curves for several levels of dissolved oxygen. As the oxygen concentration is reduced, the corrosion potential shifts in the negative direction.

The addition of either 20 ppm formic or 38 ppm oxalic acid had the same effect as a significant reduction in oxygen concentration, resulting in a more negative cathodic curve and a more negative corrosion potential. An addition of 104 ppm acetic acid had a similar effect. However, when only 26 ppm acetic acid was added, the cathodic curve and, thus, the corrosion potential were practically unaffected, indicating no significant drop in the oxygen available to interact with the specimen surface. Similar corrosion potential behavior was observed for slow-strain rate specimens exposed to these various solutions.
Figure 13. Cathodic and Anodic Polarization Curves from Ref. 17
4.6 Fractographic Examinations

To confirm the presence of intergranular stress-corrosion cracking (IGSCC) the fracture faces of the slow-strain rate specimens were examined with a scanning electron microscope. Figure 14. shows a typical specimen which had considerable intergranular crack growth before a rapid ductile final failure. This specimen (from an air saturated formic acid solution) had a relatively short failure time and the extensive secondary cracking typical of IGSCC.

In other specimens, such as #21 (shown in fig. 15.) the intergranular cracking component was totally absent. In this test (conducted in deaerated pure water) IGSCC would not have been expected and indeed none was found. Instead, most of the fracture surface was covered with the dimpled pattern associated with final ductile failure, with a small transgranular initiation region. That transgranular region is shown at higher magnification in figure 16. These transgranular crack initiation regions are probably an artifact of the slow-strain rate test, in which the continuous straining and great plastic deformation, do not duplicate actual in-reactor occurrence. In their review of stress-corrosion of type 304 stainless steel, Smialowska and Cragnoiino (24) state that there is no mention in the literature of
Figure 14. Specimen Fractograph Showing Extensive Intergranular Crack Propagation 40X
(8 ppm O₂, 20 ppm Formic Acid)
Figure 15. Specimen Fractograph Showing Transgranular Crack Propagation With Ductile Final Failure
30 X (deaerated, acid-free)
Figure 16. Enlargement of Transgranular Crack Propagation Zone 100 X
transgranular cracking in pure water in this temperature range in constant load tests. Rather, they think that transgranular cracking is limited to slow-strain rate tests.

That view is supported by the work of Yonezawa and Tsuruta (13), who conducted constant load tests in deaerated 0.025 M Na$_2$SO$_4$ at 300 C. Using a load of 1.87 yield they found no cracking at potentials below approximately -450 mV, while intergranular cracks grew rapidly above -400 mV. In the present program of slow-strain rate testing the transgranular cracks were only observed on specimens whose test potentials were below -450 mV, where no intergranular cracks were seen. Yonezawa’s work implies that under static conditions the transgranular cracking does not occur or at least does not grow to a significant extent. Cracking in a static specimen in such an environment only occurs in an intergranular mode and only at higher potentials than those at which transgranular cracking occurs in SSR tests.

Chung (14) performed crack growth rate experiments in 0.01 M Na$_2$SO$_4$ solutions at 250 C using wedge-opening-load specimens with a constant opening displacement. He found crack propagation to be strongly dependent on specimen potential, disappearing below -300 mV. Again, a statically loaded test produced no cracking in the low potential range in which transgranular cracking occurred in slow-strain rate experiments.

Extensive transgranular cracking of stainless steel is
probably restricted to very severe environments (e.g. concentrated
MgCl₂) or to dynamic, high strain experiments. Thus the
transgranular crack initiation seen in these experiments is
probably not representative of the cracking process in nuclear
reactors.

A summary of fractographic analyses, giving the fraction of
intergranular, transgranular, and ductile regions for specimens
representing each oxygen level-acid combination tested is given in:
table 15.
Table 15. Fractographic Analyses

<table>
<thead>
<tr>
<th>TEST</th>
<th>ACID</th>
<th>PPM O₂</th>
<th>FRACTION OF SURFACE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>IG</td>
</tr>
<tr>
<td>21</td>
<td>-</td>
<td>-</td>
<td>.24</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>0.2</td>
<td>.32</td>
</tr>
<tr>
<td>27</td>
<td>-</td>
<td>0.6</td>
<td>.42</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>8.0</td>
<td>.47</td>
</tr>
<tr>
<td>20</td>
<td>A</td>
<td>-</td>
<td>.23</td>
</tr>
<tr>
<td>16</td>
<td>A</td>
<td>0.2</td>
<td>.55</td>
</tr>
<tr>
<td>29</td>
<td>A</td>
<td>0.6</td>
<td>.48</td>
</tr>
<tr>
<td>12</td>
<td>A</td>
<td>8.0</td>
<td>.46</td>
</tr>
<tr>
<td>16</td>
<td>F</td>
<td>-</td>
<td>.15</td>
</tr>
<tr>
<td>14</td>
<td>F</td>
<td>0.2</td>
<td>.11*</td>
</tr>
<tr>
<td>28</td>
<td>F</td>
<td>0.6</td>
<td>.30</td>
</tr>
<tr>
<td>8</td>
<td>F</td>
<td>8.0</td>
<td>.47</td>
</tr>
<tr>
<td>30</td>
<td>O</td>
<td>-</td>
<td>.15</td>
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<td>O</td>
<td>0.2</td>
<td>.26</td>
</tr>
<tr>
<td>31</td>
<td>O</td>
<td>0.6</td>
<td>.38</td>
</tr>
<tr>
<td>32</td>
<td>O</td>
<td>8.0</td>
<td>.47</td>
</tr>
</tbody>
</table>

* Mixed intergranular and transgranular appearance

A = Acetic, F = Formic, O = Oxalic
5. DISCUSSION

Before proceeding with the discussion section, a brief review of the experimental results is presented to focus attention on the more significant findings:

1. Formic acid, at 20 ppm concentration, has no effect on stress-corrosion when the input oxygen level is 8 ppm. It has a strong inhibiting effect on cracking at 0.6 and 0.2 ppm input oxygen and a slight accelerating effect under deaerated conditions.

2. Acetic acid, in the same molarity, also has little effect with an 8 ppm oxygen concentration, but has a slight accelerating effect at 0.6 ppm. At 0.2 ppm, the stress-corrosion process is accelerated tremendously. In deaerated solutions acetic acid has a slight accelerating effect.

3. Oxalic acid exerts a slight accelerating effect at 8 ppm oxygen, while strongly inhibiting cracking at the lower oxygen levels. There appears to be no effect in oxygen-free systems.

5.1 Electrochemical Effects

One of the most surprising results of these experiments is the
stress-corrosion inhibiting effect of formic and oxalic acids at the lower oxygen levels. This behavior is quite different from what might be expected from the sulfuric acid experiments described in the literature review, where decreasing the pH decreased specimen failure times. Even more surprising is the effect of acetic acid, which in 0.2 ppm oxygen experiments produced the fastest specimen failures seen in this research, while having little effect in either air saturated or deaerated solutions. Clearly the effect of organic acids is more than a matter of simply pH or conductivity.

The basic explanation of these experimental results lies in the specimen electrode potentials, which result from the various test environments. As mentioned in the literature survey, crack propagation is strongly dependent on potential, being greatly accelerated as the potential becomes more positive. Some researchers even suggest that a threshold potential exists, below which cracking does not occur, e.g. -300 to -400 mV (SHE).

Figure 17 shows a summary of specimen potentials vs. input oxygen level for pure water and the different acid solutions used in these experiments. Also shown is Indig's (10) curve for the potential of stainless steel in pure water as a function of oxygen concentration at this temperature. In addition, the approximate range of the threshold potential for cracking, as given by various researchers, is included. This plot shows that in the experiments with strong cracking inhibition (formic and oxalic acids at low
Figure 17. Specimen Potentials vs. Inlet Oxygen Concentration
oxygen concentration) the potentials were depressed well below those of pure water solutions. In fact, the cracking behavior in all of the experiments can be correlated with this chart. Experiments in deaerated solutions produced long failure times and no evidence of intergranular attack. The potentials from these experiments (shown here as .005 ppm oxygen) all fall well below the threshold range, regardless of acid content. Experiments in air saturated solutions (8 ppm oxygen), on the other hand, all showed rapid IGSCC, which is consistent with a specimen potential well above the threshold range. The other experiments with distinct stress-corrosion cracking (pure water and acetic acid solutions at 0.2 and 0.6 ppm oxygen) also had potentials more anodic than the critical range. Thus all of the stress-corrosion behavior seen in these experiments is consistent with the electrode potentials measured during those tests. Specimens with high potentials displayed rapid failure and intergranular attack, while those at low potentials had longer failure times and no evidence of grain boundary cracking.

5.2 Effects of Formic and Oxalic acids

Having established that specimen cracking, as seen in these experiments is a function of electrode potential, the question arises: why are the potentials in 0.2 and 0.6 ppm oxygen solutions shifted negatively by formic and oxalic acids? The answer to that
question lies in the interaction between dissolved oxygen and the organic acids. In the absence of artificial electronic potential control, dissolved oxygen is the major factor in determining potential in these nearly pure, high temperature solutions. Indeed, Indig's curve shows how potential is a function of dissolved oxygen. If a foreign substance in the solution reduced the dissolved oxygen content, lower potentials would most certainly result.

Return-line dissolved oxygen measurements indicate that oxygen is consumed by the acids in this high temperature environment. Table 16 shows return-line oxygen levels as a function of both input oxygen and the acid present. The table shows that there is some oxygen consumption even in acid-free systems, especially at the 0.2 ppm input level. However the oxygen consumption is considerably greater when any of the three acids are present. At either 0.2 or 0.6 ppm input the return-line level is below the practical limits of the monitor's sensitivity if acid solutions are used. In the high temperature autoclave the following reactions may be the mechanisms for oxygen consumption:

\[
\begin{align*}
\text{HCOOH} + \frac{1}{2} \text{O}_2 & \rightarrow \text{CO}_2 + \text{H}_2 \text{O} \\
\text{CH}_3 \text{COOH} + \frac{1}{2} \text{O}_2 & \rightarrow \text{CO}_2 + \text{CH}_3 \text{OH}
\end{align*}
\]
All of these reactions have negative free energies. Other reactions may also be involved, but the net result is a decrease in oxygen concentration in the system, and a negative shift in specimen potential.

Indeed, that is precisely what occurred in the experiments where formic or oxalic acids were added to a stable high temperature system. After the acid addition, the specimen potential began to decrease along with the return-line oxygen level. Thus a cathodic shift in potential is consistent with consumption of the organic acids by dissolved oxygen.

In the low oxygen tests the concentration of formic or oxalic acid was more than sufficient to consume the oxygen present. Both acid solutions had a concentration of $4.35 \times 10^{-4}$ M while 0.6 and 0.2 ppm of dissolved oxygen correspond to $1.87 \times 10^{-5}$ M and $6.25 \times 10^{-6}$ M respectively. Thus a trivial portion of the acid present in each pass through the autoclave could have consumed the oxygen. From these concentrations one would not expect an appreciable change in pH to result from oxidation of the acids. However, output pH was generally higher than input for formic and oxalic acids, even in deaerated solutions where there was no oxygen to
Table 16. Return-Line Oxygen Levels (PPM)

<table>
<thead>
<tr>
<th>INPUT OXYGEN</th>
<th>ACID</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPM</td>
<td>NONE</td>
</tr>
<tr>
<td>0.2</td>
<td>.04-.07</td>
</tr>
<tr>
<td>.005</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>.17-.20</td>
</tr>
<tr>
<td>.005</td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>8.0</td>
</tr>
<tr>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>

All acid concentrations are $4.35 \times 10^{-4}$ molar.
react with the acids. Table 17 gives input vs. output pH for various experiments using the once-through configuration.

From these data it appears that some of the acid must decompose at high temperature, even in the absence of oxygen. As discussed in the section on high temperature thermodynamics, decomposition of formic and oxalic acids is thermodynamically favorable. The rise in pH during 0.2 and 0.6 ppm oxygen test is not significantly greater than in deaerated tests, and one would not expect it to be. However, in air saturated solutions (8 ppm or $2.5 \times 10^{-4}$ M dissolved $O_2$) there is a greater rise in pH which probably results from greater acid oxidation as well as from acid decomposition. This rise in pH during high temperature exposure was the reason that the system was converted to once-through operation, ensuring constant input pH.

Thus the cracking behavior and specimen potential for formic and oxalic acid experiments are entirely consistent with both mixed potential theory and the concept of a critical cracking potential. At 8 ppm oxygen the potential is quite high, despite some oxygen consumption by acids. Thus at that oxygen level the acids have little effect on potential or cracking. At 0.2 and 0.6 ppm the acids can effectively scavenge the oxygen, resulting in low potentials, long cracking times, and no intergranular attack.

Under deaerated conditions the potential would be low, even without any oxygen removing species. In the absence of oxygen the
Table 17. Input vs. Output Solution pH

<table>
<thead>
<tr>
<th>CONC.</th>
<th>ACID</th>
<th>INPUT PH</th>
<th>OUTPUT PH</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;.005</td>
<td>Oxalic</td>
<td>3.3</td>
<td>4.2</td>
</tr>
<tr>
<td>0.2</td>
<td>Formic</td>
<td>3.5</td>
<td>4.0</td>
</tr>
<tr>
<td>0.2</td>
<td>Oxalic</td>
<td>3.3</td>
<td>4.4</td>
</tr>
<tr>
<td>0.6</td>
<td>Formic</td>
<td>3.5</td>
<td>4.0</td>
</tr>
<tr>
<td>0.6</td>
<td>Oxalic</td>
<td>3.4</td>
<td>4.2</td>
</tr>
<tr>
<td>8.0</td>
<td>Formic</td>
<td>3.4</td>
<td>4.7</td>
</tr>
<tr>
<td>8.0</td>
<td>Oxalic</td>
<td>3.5</td>
<td>4.7</td>
</tr>
</tbody>
</table>
acid solutions have slightly higher potentials than pure water because of proton reduction. That higher potential seems to have slightly accelerated cracking in formic acid solutions, while having little effect in oxalic acid (in formic acid the potential rise was greater).

5.3 Effects of acetic acid

Although the behavior of formic and oxalic acids can be readily explained in terms of oxygen scavenging, the effects of acetic acid are not so clear. Acetic acid, in the same molarity as the other two acids, had little effect at 8 ppm or 0.6 ppm oxygen compared to pure water. Likewise, in deaerated solutions the acetic acid effect was also negligible. At 0.2 ppm, however, the cracking process was the fastest seen in any experiment, giving specimen failure in half the time of acid-free tests. Perhaps the answer for the questions raised by the acetic acid experiments lies in the cathodic polarization curves (described in the results section). The curves for formic acid, with or without 0.6 ppm oxygen, show essentially no oxygen effect. Both have very low corrosion potentials and nearly identical current values at the higher cathodic overpotentials. The oxygenated oxalic acid curve is similar. Thus for those acids, 0.6 ppm of oxygen was consumed rapidly enough to prevent it from playing any role in controlling specimen potential. The curve for 26 ppm acetic acid at that
oxygen content has much higher potential values, indicating that some free oxygen was available for reduction on the specimen surface. Although much of the oxygen was consumed by the acid, there must have been enough left over to polarize the specimen anodically.

The observation that the return line oxygen was nearly zero in both acetic and formic acids can be explained as follows: Oxygen can be eliminated by either reactions with the vessel and specimen or by reactions with the acid (which may occur on the metallic surfaces). In formic acid environments the bulk of oxygen elimination is probably by reaction with the acid, while with acetic acid reactions with the stainless steel surfaces play a major role. Both routes yield low return line oxygen levels, but the latter process would lead to higher specimen potential, because electrons from the alloys are involved.

For this theory to be valid, acetic acid must be a less effective oxygen scavenger than the other two. Thus raising the acetic acid level sufficiently might produce a polarization curve resembling those of 20 ppm formic acid or 36 ppm oxalic acid. A fourfold increase in acetic acid concentration accomplished just that, yielding a curve with a more negative corrosion potential and polarization response, like that of the lower molarity formic and oxalic solutions. Therefore, from these experiments it may be concluded that formic and oxalic acids produce lower specimen.
potentials and longer cracking times than acetic acid (in low oxygen solutions) because they are more effective oxygen consumers.

Such a premise leaves two unanswered questions: why is acetic acid less effective at removing oxygen and why is cracking so severe in the acetic acid-0.2 ppm O\textsubscript{2} combination? The answer to the first question may lie in the acidity of the various solutions. Table 4 gives the dissociation constants for the three acids at 25 and 275 C, while Table 5 gives pH values for the test solutions at the same temperatures. The room temperature values are from standard chemistry tables (4), while the elevated temperature values were calculated by techniques described in the section on high temperature thermodynamics. In the pH calculations the second dissociation of oxalic acid was considered negligible.

These tables clearly show that acetic acid is weakest (lowest K) of the three and yields the highest pH at 275 C. If the dissociated organic anion (formate, acetate, or oxalate) rather than the undissociated molecule is responsible for oxygen consumption, then the effects of the different acids can be explained in terms of pH. For the three equimolar solutions (20 ppm formic, 26 ppm acetic, and 38 ppm oxalic) the pH of acetic is by far the highest. Thus at 275 C the acetic acid solution has approximately 20 \% of the dissociated organic species as formic acid, resulting in considerably less oxygen reduction. Raising the acetic acid concentration fourfold to 104 ppm yields a pH of 4.5 at
275 °C, which corresponds to approximately 40% of the dissociated organic concentration found in the formic solution. That increase appears to be enough to essentially eliminate oxygen from the potential control process, according to the polarization curves. The curve for 104 ppm acetic acid resembles the formic acid curves, which have very low corrosion potentials.

Since the exact mechanism of organic acid oxidation in high temperature solutions is not known, the preceding discussion must be regarded as a theory; however it will explain the observed effects of the various acids on oxygen consumption and potential control.

The remaining question is why acetic acid causes such severe cracking at 200 ppb of dissolved oxygen, as compared to higher or lower levels. That question cannot be answered based on the present information, and would be an interesting subject for future research.
6. CONCLUSIONS

1. Stress-Corrosion cracking of type 304 stainless steel in aqueous solutions at 275°C is critically dependent on electrode potential, which in turn is dependent on the availability of dissolved oxygen.

2. At concentrations of 20 and 38 ppm, respectively, formic and oxalic acids effectively consume dissolved oxygen leading to more negative potentials and inhibition of stress-corrosion.

3. Acetic acid is a much less effective oxygen consumer than formic or oxalic acids, requiring higher concentrations to achieve the same oxygen suppression. In lower concentrations acetic acid accelerates stress-corrosion cracking.
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