VOLUMETRIC DETERMINATION OF INORGANIC SULFUR-BEARING REDUCING COMPOUNDS IN ALKALINE PULPING SOLUTIONS

INTRODUCTION

Project 1887, originally established by the Institute on July 25, 1955 to study the "corrosion of mild steel by neutral and alkaline pulping solutions", has since developed into a jointly sponsored (TAPPI-Institute) program through the reception of TAPPI Research Grant 86. The stated objective of the project is "a laboratory study of the corrosive behavior of the electrolytes, individually and collectively, present in alkaline pulping solutions".

A prerequisite for such a study is a reasonably accurate knowledge of the absolute concentrations of the compounds present in the solutions in question, and such knowledge is gained from the results of a chemical analysis of the solutions. In view of the importance of chemical analysis in the projected study, a review of the major existing methods of analysis was made. From this review came the decision to attempt to adapt, in the laboratory, some of the existing methods to a general procedure that would apply to all the solutions to be used in the corrosion study. The compounds of interest in this respect are those sodium-sulfur compounds that may be oxidized to sulfate, viz., sulfide, polysulfides, thiosulfate, and sulfite. Sulfate is usually present in alkaline pulping liquors to a small extent, but its determination (gravimetric as BaSO₄) generally presents no problem.
The polysulfide sulfur in Na$_2$Sn, represented by n-1 is the constituent for which there appears to be no definite method of determination when it is present in alkaline pulping liquors. The work recorded in this report was conducted with the intention that it would result in a practical, rapid, and fairly accurate method for the determination of polysulfide sulfur in alkaline pulping liquors.

DISCUSSION OF EXISTING METHODS

In a survey of the literature, no method of analysis for polysulfide sulfur was found that had been applied to alkaline pulping liquors and met the requirements of speed, simplicity, and accuracy to the satisfaction of the investigators involved in this project. Many methods were found, however, that had been applied with apparent success to various liquors used outside the pulp and paper industry. Other methods for the determination of sulfide, sulfite, and thiosulfate in the presence of each other ignored the possibility of the presence of polysulfides and/or were questionable as to stated accuracy and ease of application.

Tappi Method T624 m-44 for the determination of sulfide, sulfite, and thiosulfate in the presence of each other has often been under criticism (1, 2). It has been the experience in this laboratory that the use of this method gives rise to gross inaccuracies for both sulfite and thiosulfate. The supporting data are contained in the experimental section of this report.

Murthy's (2, 3) method for determining sulfide, sulfite, and thiosulfate in a mixture of the three appeared at first to be a simple and accurate method, but upon laboratory trial of the method, difficulties were experienced with the oxidation of sulfide and with certain manual operations required by the procedure. It was found, however, that a good degree of accuracy could be obtained in the determination of thiosulfate and sulfite. This method
depends upon the quantitative oxidation of all sulfur compounds to sulfate; Chloramine-T in acid medium being the oxidizing agent. Since difficulty was experienced with the quantitative oxidation of sulfide, it was felt that this method offered little possibility for the development of a method for polysulfides. Supporting data are contained in the experimental section of this report.

The hypohalogens have been used extensively for the determination of sulfur compounds. Willard and Cake (4) studied the use of sodium hypobromite and hypochlorite in the determination of sulfides. Kolthoff and Sandell (5) report that in alkaline medium sulfide, sulfite, and thiosulfate are quantitatively oxidized to sulfate by calcium hypochlorite. Sheintsis (6) used calcium hypochlorite to determine thiosulfate and sulfite in alkaline medium. Abel (7) found that thiosulfate could be determined quantitatively by iodine in alkaline medium (hypoiodite). Kolthoff (8) also used alkaline iodine in the determination of thiosulfate.

Choppin and Falkenberry (9) made a thorough study of the mechanism of, and the conditions necessary for, quantitative oxidation of aqueous sulfide solutions by hypochlorites.

Bodnar and Gervay (10) made a review and critical analysis of the then existing methods for the determination of polysulfide sulfur and proposed a new titrimetric method of their own. This work is apparently the basis for most methods for polysulfides used today, very little having been done since. Of the methods discussed in the Bodnar and Gervay publication, none were quite satisfactory, for various reasons, for application to alkaline pulping solutions.
EXPERIMENTAL

A perusal of the literature mentioned above led to the belief that, in an analytical procedure for the determination of sulfide, sulfite, thiosulfate and polysulfide sulfur, the most advantageous combination of the factors of accuracy, simplicity of procedure, and speed could best be obtained in a volumetric method incorporating an oxidizing agent that would quantitatively oxidize to sulfate all the sulfur compounds involved. Chloramine-T and the hypohalogen ions have been used by others as oxidizers in volumetric oxidimetry, but no data has been found to support a supposition that these agents will quantitatively oxidize to sulfate all the sulfur compounds present in a mixture of sulfide, polysulfide, sulfite, and thiosulfate. It was to support such a supposition that the following work was undertaken. Methods used to standardize the various solutions of sulfur compounds used will be found in the appendix.

I. Chloramine-T

Chloramine-T derives its power as an oxidizing agent from the liberation of nascent oxygen in acid medium.

\[
\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NClNa} + \text{H}_2\text{O} = \text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NH}_2 + \text{NaCl} + \text{O}
\]  

and, in acid medium will, according to Murthy (2) quantitatively oxidize sulfide, sulfite, and thiosulfate to sulfate

\[
4\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NClNa} + \text{Na}_2\text{S} + 4\text{H}_2\text{O} = 4\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NH}_2 \\
+ \text{Na}_2\text{SO}_4 + 4\text{NaCl}
\]  

4\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NClNa} + \text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O} = 4\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NH}_2 \\
+ \text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + 4\text{NaCl}
\]  

\[
\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NClNa} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} = \text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NH}_2 \\
+ \text{Na}_2\text{SO}_4 + \text{NaCl}
\]
The method used by Murthy involves two titrations with standard 0.1 N Chloramine-T; one to determine the total reducing power of the unknown solution (x) and another to determine the sulfide by oxidation of the precipitated cadmium sulfide (y); and one titration with standard iodine in acid medium to determine the reducing power of the solution after precipitation and removal of the sulfide (z). If a, b, and c represent the number of moles of sulfide, sulfite, and thiosulfate present in the unknown, then

\[ 8a + 2b + 8c = x \]  \hspace{1cm} (a)

\[ 8a = y \]  \hspace{1cm} (b)

\[ 2b + c = z \]  \hspace{1cm} (c)

and the values of a, b, and c can be calculated.

A modification of this method has been used in this laboratory for about a year for the determination of sulfite and thiosulfate (see Project Report 6, May 10, 1955, Project 1568).

It was felt that if Chloramine-T could quantitatively oxidize sulfide to sulfate, the same would be true for any polysulfide sulfur present. A standard solution of sodium sulfide which was analyzed for sulfide, sulfite, and thiosulfate content was added by aliquots to excess standard Chloramine-T following Murthy's procedure. Since this procedure did not produce satisfactory results, several other procedures calculated to improve the results were tried. No procedure was found that would give reasonably accurate results in the oxidation of sulfide to sulfate by Chloramine-T. See Table I.

II. Calcium Hypochlorite and Hypobromite

According to Köthoff and Sandell (5) calcium hypochlorite in alkaline medium quantitatively oxidizes sulfide, sulfite, and thiosulfate to sulfate. Again, it was thought that if that were true for the above mentioned compounds,
it would also apply to any polysulfide present in the mixture.

An 0.15 N solution of calcium hypochlorite was made and filtered until a clear solution was obtained. It was found that the solution required standardizing every day. Hypobromite was prepared from the hypochlorite solution by dissolving excess potassium bromide in the hypochlorite.

A number of titrations were made with both hypochlorite and hypobromite on a standard sodium sulfide solution which was analyzed for sulfide, sulfite, and thiosulfate content. In general the procedure used was as follows: To a glass-stoppered 250 ml. Erlenmeyer flask containing a substantial excess of oxidant, was added an aliquot of the sulfide solution followed by a definite amount of strong alkali, or, in one case, sodium bicarbonate. The mixture was allowed to stand for a definite length of time, then the excess oxidant was determined by dissolving excess potassium iodide in the mixture, acidifying, and titrating the liberated iodine with standard 0.1 N sodium thiosulfate.

In one case, the titrations were carried out in acid medium in a sealed evacuated flask according to the following procedure: Evacuate a Shaw sulfide flask to minimum pressure with a water aspirator. Add the aliquots of unknown, oxidant, and excess 20% sulfuric acid to the flask in that order, and shake the flask for a few minutes. Next add an excess of 10% potassium iodide to the flask, remove the sealing stopper and titrate the liberated iodine with standard 0.1 N sodium thiosulfate.

The results (see Table II) were not very good, due, probably to insufficient alkali during the oxidation reaction. When sodium hydroxide is added to a solution of calcium hypochlorite, calcium is precipitated as the hydroxide.
Ca^{++} + 2OCl^- + 2Na^+ + 2OH^- = Ca(OH)_2 \downarrow + 2Na^+ + 2OCl^- \quad (5)

and in order to obtain the concentration of hydroxyl ions necessary to promote the oxidation reaction, the amount of alkali added must be the amount required to obtain the desired concentration plus that necessary for precipitation of the calcium. Thus, an excessive amount of sodium hydroxide is demanded when using calcium hypochlorite as an oxidant. The disadvantage of this is clear when the solution is acidified in the procedure for determining the excess oxidant. A large amount of hydrochloric acid is required and with the neutralization a large amount of heat is liberated which could result in loss of iodine by volatilization.

The solution could, of course, be pre-cooled in ice-water, but the procedure would still involve an excessive consumption of sodium hydroxide and hydrochloric acid. In addition, the solution is opaque and muddy with precipitated calcium salts during the oxidation and the analyst is not able to determine visually whether or not any free sulfur remains un-oxidized in suspension. For these reasons calcium hypochlorite and hypobromite were discarded as oxidizing agents.

III. Sodium hypochlorite and hypobromite

Choppin and Falkenberry (9) made an extensive investigation into the mechanism of the oxidation of sulfide by hypochlorites, and proposed the conditions necessary for the reaction to proceed quantitatively. For the over-all oxidation reaction between sulfide and hypochlorite

$$Na_2S + 4 NaOCl = Na_2SO_4 + 4 NaCl \quad (6)$$

they proposed the initial reaction

$$Na_2S + NaOCl + H_2O = S + NaCl + 2 NaOH \quad (7)$$
followed by the following step-wise reactions

\[
S + NaOCl = SO + NaCl \quad (8)
\]
\[
SO + H_2O = H_2SO_2 \quad (9)
\]
\[
H_2SO_2 + NaOCl = H_2SO_3 + NaCl \quad (10)
\]
\[
H_2SO_3 + NaOCl = H_2SO_4 + NaCl \quad (11)
\]

They found that the hydroxyl ion concentration is important by keeping the sulfur, formed in (7), in solution, and at a limiting hydroxyl ion concentration of 3N the sulfur is dissolved as fast as it is formed

\[6NaOH + 8S = 2Na_2S_3 + Na_2S_2O_3 + 3H_2O \quad (12)\]

By analogy with the mechanism proposed for sulfide, the corresponding mechanism may be derived for thiosulfate

\[Na_2S_2O_3 + NaOCl = Na_2SO_4 + S + NaCl \quad (13)\]

followed by reactions (8), (9), (10), and (11), the over-all reaction for which may be expressed

\[Na_2S_2O_3 + 4NaOCl + H_2O = Na_2SO_4 + H_2SO_4 + 4NaCl \quad (14)\]

sulfite

\[Na_2SO_4 + NaOCl = Na_2SO_3 + NaCl \quad (15)\]

and sulfur (polysulfide) would be the same as reactions (8), (9), (10), and (11) with the over-all reaction

\[S + 3NaOCl + H_2O = H_2SO_4 + 3NaCl \quad (16)\]

Willard and Cake (4) found that for the quantitative oxidation of sulfide to sulfate with hypochlorite a minimum hydroxyl ion concentration of 4N was required, and with hypobromite the concentration must be 2.5 N.

A solution of sodium hypochlorite approximately 0.3N was prepared by dissolving the proper amount of calcium hypochlorite in water, and adding sodium hydroxide in slight excess of the amount necessary to precipitate all the calcium as calcium hydroxide. The mixture was filtered clear and diluted with distilled water to give the concentration desired. The solution was standardized
daily in the same manner as the calcium hypochlorite mentioned previously.

Sodium hypobromite solution was prepared in two ways: by adding excess potassium bromide to the standard hypochlorite solution, and by dissolving thirty grams of liquid bromine in one liter of normal sodium hydroxide. The first method gives a solution of known hypobromite concentration and the second gives a solution of about 0.3 N which requires standardization.

The first step in the investigation of sodium hypochlorite and hypobromite as volumetric oxidizing agents was to confirm the reports of other writers (4, 9) that the oxidation of sulfide, sulfite, and thiosulfate proceeds quantitatively under specified conditions. A standard solution of sodium sulfide was analyzed for sulfide, sulfite, and thiosulfate content and aliquots of this known solution were titrated with the two oxidants according to the procedure of Willard and Cake (4). See Table III for results.

Since the initial results were satisfactory it was decided to try to extend the method, standardize the technique, set the conditions and to reduce the error. At this point it was decided to eliminate the use of hypobromite, because both hypochlorite and hypobromite appeared to give substantially the same results.

Experiments were next conducted on sulfite and thiosulfate solutions individually and in known mixtures of the two. When sulfite and thiosulfate are present in a mixture and no other reducing substances are present, thiosulfate is oxidized to sulfate by hypochlorite according to equation (14) and sulfite goes to sulfate according to equation (15). Thus, thiosulfate requires eight oxidizing equivalents per mole and sulfite requires two. When the mixture is titrated with standard iodine in acid medium, thiosulfate is oxidized to tetrathionate and sulfite to sulfate; thiosulfate requiring one
oxidizing equivalent per mole and sulfite two.

\[ 2\text{Na}_2\text{S}_2\text{O}_3 + I_2 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \]  
(17)

\[ \text{Na}_2\text{SO}_3 + I_2 + \text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + 2\text{HI} \]  
(18)

Thus, if \( a \) and \( b \) represent thiosulfate and sulfite, respectively, in gram-moles per liter, \( x \) represents equivalents per liter found by a hypochlorite titration, and \( y \) is equivalents per liter found by an acidic iodine titration, then

\[ 8a + 2b = x \]  
(d)

\[ a + 2b = y \]  
(e)

and the respective concentrations of thiosulfate and sulfite may be calculated.

When thiosulfate alone and sulfite alone are titrated with hypochlorite the results in equivalents per liter are divided by eight and two respectively to obtain the results in gram-moles per liter.

The results of the titrations described above are recorded in Table IV.

It can be seen from Table IV that when a pure thiosulfate solution is titrated with sodium hypochlorite at an alkalinity above 4 N with respect to hydroxyl ions, the maximum error is about six-tenths of one per cent, and the average error is about four-tenths of one per cent. For sulfite the maximum error appears to be about seven-tenths of one per cent at a hydroxyl ion concentration of about 3 N, and an average error of about four-tenths. These errors all have a negative nature.

When sulfite and thiosulfate are present together in a solution, the error for thiosulfate appears to be close to plus or minus one per cent, while sulfite still has a negative error, in this case about seven-tenths per cent.

That these errors for the individual compounds are not entirely cumulative can be seen from Table III where a solution was titrated with sodium
hypochlorite that contained sulfide, sulfite and thiosulfate. The direction of the error is still negative, with a maximum value of about three-quarters of one per cent of the total reducing equivalents present. The average error for the series of titrations is a little over one-half per cent.

Having established that the oxidation of sulfide, sulfite, and thiosulfate by sodium hypochlorite in alkaline medium is quantitative within an acceptable margin of error, the next step in the evolution of the method was to prepare a polysulfide solution of known sulfur content. The prepared solution would then be analyzed for all sulfur compounds including polysulfide sulfur. Two such polysulfide solutions were prepared in the following manner:

A sodium sulfide solution was prepared and analyzed for sulfide, sulfite, thiosulfate, and sulfate content. Total sulfur was determined independently by the standard gravimetric method and the result compared with the sum of the sulfur as determined in the individual compounds. An aliquot of this known solution was measured into a two-neck round-bottom flask, and an accurately weighed amount of U.S.P. sublimed sulfur was added. To the central neck of the flask was attached a reflux condenser, and to the open end of the condenser was attached a small gas washing bottle containing about 15 ml. normal sodium hydroxide to trap any gases evolved. To the side-neck of the flask was attached a cylinder of compressed nitrogen. The flask was heated by a Glass-col heating mantle controlled by a Variac. Before heating the flask, all air was flushed from the apparatus by slowly passing nitrogen through it for about fifteen minutes. The flask was then heated until the contents reached the boiling point, and gentle boiling was continued until all the sulfur was seen to be dissolved. Nitrogen was slowly, but continuously, passed through the apparatus until the solution was removed from the flask.
As soon as the solution reached room temperature, it was analyzed for sulfide, sulfite, thiosulfate, sulfate, polysulfide sulfur, and total sulfur content. See Table V for the results.

The figures for "total sulfur (grav.)" in the table refer, in the case of the sulfide solution, to an independent gravimetric determination of the total sulfur content of the solution before adding any sulfur and was used as a check on the total sulfur summation expressed in the table as "total_1". The figures for "total_2" refer to the sum total of all the sulfur in the solution after addition of the elemental sulfur to the sulfide solution. In the case of the sulfide solution the figure is obtained by totaling the sulfur weighed out and "total_1". In the polysulfide solution the figure for "total_2" represents the sum of the sulfur content of the individual constituents determined by analysis. "Total_1" and "total sulfur (grav.)" for the sulfide solution should be the same. "Total_2" sulfide solution, "total_2" polysulfide solution, and "total sulfur (grav.)" polysulfide solution should all be the same. The error was calculated as the difference between the two "total_2" figures over "total_2" sulfide solution.

It can be seen from the data in Table V that the volumetric method involves a rather consistent negative error of about one and one-half per cent of the total sulfur involved. If, however, the polysulfide sulfur present in the solution is taken as the difference between the sulfur found by a total sulfur determination and the sulfur found by a summation of the sulfur content of the sulfide, sulfite, sulfate, and thiosulfate present, the error is reduced to less than two-tenths per cent of the total sulfur involved.

The volumetric method of determining polysulfide sulfur is rapid and does not require a knowledge of the sulfate content, but involves a negative error of about one and one-half per cent of the total sulfur.
gravimetric method requires a knowledge of the sulfate content and involves two lengthy gravimetric determinations, but gives results accurate to within two-tenths of one per cent of the total sulfur.

When a liquor is analyzed volumetrically for the sulfide, sulfite, thiosulfate, and polysulfide sulfur, the results may be had within two and one-half hours. If the gravimetric method for polysulfide sulfur is used, about thirty-six hours is required before the results are at hand.

IV. Alkaline Iodine (Sodium hypoiodite)

At an alkalinity above pH 8 iodine reacts with hydroxyl ions to form hypoiodite and iodide, but the hypoiodite is unstable and is very rapidly transformed into iodate and iodide (11)

\[
I_2 + 2OH^- = OI^- + I^- + H_2O
\]  
(19)

\[
3O^- = 2I^- + IO_3^- \]  
(20)

Iodine in alkaline medium oxidizes thiosulfate to sulfate (12) presumably by the same reaction mechanism reported previously for hypochlorite. Abel (7) employed this reaction in a quantitative method for determining thiosulfate.

If thiosulfate undergoes quantitative oxidation to sulfate by alkaline iodine, so, was the assumption, should sulfide, sulfite, and polysulfide sulfur, the reaction mechanisms and the over-all reactions being similar to the same reactions with hypochlorite.

Since hypoiodite is extremely unstable, it was thought that the reaction could best be promoted by adding slowly a neutral solution of standard iodine to the titrating flask already containing the sulfur compounds to be oxidized and the sodium hydroxide solution. This procedure was followed in all the titrations carried out with iodine in alkaline medium.
Table VI contains the data obtained in a series of titrations made upon a standard thiosulfate solution with iodine at various hydroxyl ion concentrations. The purpose of the series was to determine the minimum hydroxyl ion concentration necessary for complete oxidation of thiosulfate to sulfate.

Table VII contains the data obtained in a series of determinations made on known mixtures of thiosulfate and sulfite. Two titrations were made on each mixture, one with iodine in acid medium, and one with iodine in alkaline medium. The respective concentrations of sulfite and thiosulfate were calculated as before when using hypochlorite.

Table VIII is a comparison of two methods of analysis for the same compounds. The liquor analyzed was an exit liquor from the conversion unit used in this laboratory in investigations of neutral sulfite chemicals recovery methods. Specifically, it was the exit liquor of Run 4, Project 1568, January 13, 1956. The liquor contained hydrosulfide, sulfite, thiosulfate, carbonate and bicarbonate ions, and, of course, small amounts of sulfate.

The liquor was analyzed for hydrosulfide, sulfite, and thiosulfate by one analyst according to the method listed in the appendix for standardizing a solution containing sulfide, sulfite, and thiosulfate, and by this analyst using iodine as the sole oxidizing reagent in both acid and alkaline medium according to the procedure experimentally determined in this report. When sulfide is present, a much higher hydroxyl ion concentration, about 6 N, is required for quantitative oxidation to sulfate.

Table IX presents the results of an analysis of a polysulfide solution of known sulfur content by the iodometric method. The polysulfide solution analyzed was the same solution made and reported in Table V, trial II. The
solution had been stored in the absence of light and air, and still contained appreciable polysulfide as evidenced by its very yellow color. The accuracy obtained was a plus one and three-tenths per cent of the total sulfur in the solution. Again, an estimation of the polysulfide sulfur by means of gravimetric method is of a high order of accuracy; in this case a deviation of less than a tenth of a per cent of the total sulfur involved is achieved.

In Table VI, VII, and VIII, the figures for the hydroxyl ion concentration at the end of the titration are expressed in terms of normality and are calculated by dividing the sum of the volumes of iodine, sodium hydroxide solution, and the aliquot of solution of reducing compounds by the equivalents of hydroxyl ion added.
### TABLE I

**OXIDATION OF SULFIDE TO SULFATE WITH CHLORAMINE-T**

**Standard Na₂S Solution**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Gram-moles per liter</th>
<th>Calculated Chloramine-T reducing equivalents per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S</td>
<td>0.239</td>
<td>1.912</td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>0.005</td>
<td>0.040</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>0.016</td>
<td>0.032</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>1.984</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total Chloramine-T reducing equivalents per liter found</th>
<th>Error, equivalents per liter</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Murthy's procedure:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(aliquot added to excess oxidant before acidification)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) 1.868</td>
<td>0.116</td>
<td>- 5.8</td>
</tr>
<tr>
<td>2) 1.876</td>
<td>0.108</td>
<td>- 5.5</td>
</tr>
<tr>
<td>3) 1.894</td>
<td>0.090</td>
<td>- 4.5</td>
</tr>
<tr>
<td>B. Aliquot added to acidified oxidant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) 1.848</td>
<td>0.136</td>
<td>- 6.9</td>
</tr>
<tr>
<td>2) 1.821</td>
<td>0.153</td>
<td>- 7.7</td>
</tr>
<tr>
<td>C. Oxidation carried out in sealed evacuated flask</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) 1.806</td>
<td>0.178</td>
<td>- 9.0</td>
</tr>
<tr>
<td>2) 1.820</td>
<td>0.164</td>
<td>- 8.3</td>
</tr>
<tr>
<td>3) 1.908</td>
<td>0.076</td>
<td>- 3.8</td>
</tr>
</tbody>
</table>
### TABLE II
OXIDATION OF SULFIDE TO SULFATE WITH CALCIUM HYPOCHLORITE AND HYPOBROMITE

Standard Na₂S Solution

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Gram-moles per liter</th>
<th>Calculated OCl⁻ and OBr⁻ reducing equivalents per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S</td>
<td>0.236</td>
<td>1.888</td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>0.017</td>
<td>0.034</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>0.006</td>
<td>0.048</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>1.970</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total reducing equivalents per liter found</th>
<th>Error, equivalents per liter</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Hypochlorite-no alkali added</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) 1.040</td>
<td>0.930</td>
<td>-47.2</td>
</tr>
<tr>
<td>2) 1.058</td>
<td>0.912</td>
<td>46.3</td>
</tr>
<tr>
<td>3) 1.071</td>
<td>0.899</td>
<td>45.6</td>
</tr>
<tr>
<td>B. Hypochlorite-in bicarbonate medium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) 1.752</td>
<td>0.218</td>
<td>11.1</td>
</tr>
<tr>
<td>2) 1.837</td>
<td>0.133</td>
<td>6.8</td>
</tr>
<tr>
<td>3) 1.878</td>
<td>0.092</td>
<td>4.7</td>
</tr>
<tr>
<td>C. Hypochlorite-definite amounts 8N NaOH added</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) 1.087</td>
<td>0.883</td>
<td>44.8</td>
</tr>
<tr>
<td>2) 1.094</td>
<td>0.876</td>
<td>44.5</td>
</tr>
<tr>
<td>3) 1.109</td>
<td>0.861</td>
<td>43.7</td>
</tr>
<tr>
<td>D. Hypochlorite-in strongly acid medium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) 1.620</td>
<td>0.350</td>
<td>17.8</td>
</tr>
<tr>
<td>2) 1.618</td>
<td>0.352</td>
<td>17.9</td>
</tr>
<tr>
<td>E. Hypobromite-definite amounts 8N NaCl added</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) 1.081</td>
<td>0.889</td>
<td>45.1</td>
</tr>
<tr>
<td>2) 1.113</td>
<td>0.957</td>
<td>48.6</td>
</tr>
<tr>
<td>3) 1.126</td>
<td>0.844</td>
<td>42.8</td>
</tr>
</tbody>
</table>
### TABLE III

**OXIDATION OF SULFIDE TO SULFATE WITH SODIUM HYPOCHLORITE AND HYPOBROMITE**

Standard \( \text{Na}_2\text{S} \) Solution

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Gram-moles per liter</th>
<th>Calculated ( \text{OCl}^- ) and ( \text{OBr}^- ) reducing equivalents per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Na}_2\text{S} )</td>
<td>0.2292</td>
<td>1.8336</td>
</tr>
<tr>
<td>( \text{Na}_2\text{S}_2\text{O}_3 )</td>
<td>0.0048</td>
<td>0.0384</td>
</tr>
<tr>
<td>( \text{Na}_2\text{SO}_3 )</td>
<td>0.0125</td>
<td>0.0250</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>1.8970</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total reducing equivalents per liter found</th>
<th>Error, equivalents per liter</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. Hypochlorite</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) 1.8827</td>
<td>0.0143</td>
<td>-0.75</td>
</tr>
<tr>
<td>2) 1.8825</td>
<td>0.0145</td>
<td>-0.76</td>
</tr>
<tr>
<td>3) 1.8908</td>
<td>0.0062</td>
<td>-0.33</td>
</tr>
<tr>
<td>4) 1.8896</td>
<td>0.0074</td>
<td>-0.39</td>
</tr>
<tr>
<td><strong>B. Hypobromite</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) 1.8852</td>
<td>0.0118</td>
<td>-0.62</td>
</tr>
<tr>
<td>2) 1.8800</td>
<td>0.0170</td>
<td>-0.90</td>
</tr>
<tr>
<td>3) 1.8766</td>
<td>0.0204</td>
<td>-1.07</td>
</tr>
<tr>
<td>4) 1.8847</td>
<td>0.0123</td>
<td>-0.65</td>
</tr>
</tbody>
</table>
TABLE IV

A. Oxidation of thiosulfate to sulfate with sodium hypochlorite in alkaline medium

<table>
<thead>
<tr>
<th>Conc. known Na$_2$S$_2$O$_3$ solution, gram moles per liter</th>
<th>Conc. found, moles per liter</th>
<th>NaOH conc. at end of titration</th>
<th>Error, gram moles per liter</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1004</td>
<td>0.0994</td>
<td>1.3 N</td>
<td>0.0010</td>
<td>-1.0</td>
</tr>
<tr>
<td>0.1004</td>
<td>0.0996</td>
<td>2.4 N</td>
<td>0.0008</td>
<td>-0.8</td>
</tr>
<tr>
<td>0.1004</td>
<td>0.0999</td>
<td>4.0 N</td>
<td>0.0005</td>
<td>-0.5</td>
</tr>
<tr>
<td>0.1004</td>
<td>0.1002</td>
<td>4.5 N</td>
<td>0.0002</td>
<td>-0.2</td>
</tr>
<tr>
<td>0.1004</td>
<td>0.0998</td>
<td>5.0 N</td>
<td>0.0006</td>
<td>-0.6</td>
</tr>
</tbody>
</table>

B. Oxidation of sulfite to sulfate with sodium hypochlorite in alkaline medium

<table>
<thead>
<tr>
<th>Conc. known Na$_2$S$_2$O$_3$ solution, gram moles per liter</th>
<th>Conc. found, moles per liter</th>
<th>NaOH conc. at end of titration</th>
<th>Error, gram moles per liter</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3932</td>
<td>0.3927</td>
<td>3.0 N</td>
<td>0.0005</td>
<td>-0.1</td>
</tr>
<tr>
<td>0.3932</td>
<td>0.3905</td>
<td>2.9 N</td>
<td>0.0027</td>
<td>-0.7</td>
</tr>
</tbody>
</table>

C. Determination of sulfite and thiosulfate in mixtures of the two with alkaline sodium hypochlorite and acidic iodine

<table>
<thead>
<tr>
<th>Taken, Na$_2$S$_2$O$_3$, gram moles per liter</th>
<th>Found, Na$_2$SO$_3$, gram moles per liter</th>
<th>NaOH conc. at end of NaOCl titration</th>
<th>Error, Na$_2$S$_2$O$_3$, gram moles per liter</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$S$_2$O$_3$</td>
<td>0.0502</td>
<td>4.4 N</td>
<td>0.0005</td>
<td>+1.0</td>
</tr>
<tr>
<td>Na$_2$SO$_3$</td>
<td>0.1955</td>
<td></td>
<td>0.0011</td>
<td>-0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Taken, Na$_2$S$_2$O$_3$, gram moles per liter</th>
<th>Found, Na$_2$SO$_3$, gram moles per liter</th>
<th>NaOH conc. at end of NaOCl titration</th>
<th>Error, Na$_2$S$_2$O$_3$, gram moles per liter</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$S$_2$O$_3$</td>
<td>0.0502</td>
<td>4.4 N</td>
<td>0.0003</td>
<td>-1.2</td>
</tr>
<tr>
<td>Na$_2$SO$_3$</td>
<td>0.2895</td>
<td></td>
<td>0.0027</td>
<td>-0.9</td>
</tr>
</tbody>
</table>
#### TABLE V

DETERMINATION OF POLYSULFIDE SULFUR WITH ALKALINE SODIUM HYPOCHLORITE

**Trial I**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>gram moles</th>
<th>S</th>
<th>gram moles</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S</td>
<td>0.0463</td>
<td>0.0463</td>
<td>0.0457</td>
<td>0.0457</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>0.0024</td>
<td>0.0024</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>0.0011</td>
<td>0.0022</td>
<td>0.0042</td>
<td>0.0084</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.0006</td>
<td>0.0006</td>
<td>0.0011</td>
<td>0.0011</td>
</tr>
<tr>
<td>Total₁</td>
<td></td>
<td>0.0515</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur added</td>
<td>0.0063</td>
<td>0.0063</td>
<td>0.0018</td>
<td>0.0018</td>
</tr>
<tr>
<td>&quot;poly&quot; sulfur</td>
<td></td>
<td></td>
<td>0.0018</td>
<td>0.0018</td>
</tr>
<tr>
<td>Total₂</td>
<td></td>
<td>0.0578</td>
<td>0.0570</td>
<td></td>
</tr>
<tr>
<td>Total sulfur (grav.)</td>
<td>0.0514</td>
<td>0.0577</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

error = \( \frac{0.0578 - 0.0570}{0.0578} \times 100 = -1.4\% \)

**Trial II**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>gram moles</th>
<th>S</th>
<th>gram moles</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S</td>
<td>0.1156</td>
<td>0.1156</td>
<td>0.1146</td>
<td>0.1146</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>0.0062</td>
<td>0.0062</td>
<td>0.0002</td>
<td>0.0002</td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>0.0026</td>
<td>0.0052</td>
<td>0.0112</td>
<td>0.0224</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.0014</td>
<td>0.0014</td>
<td>0.0018</td>
<td>0.0018</td>
</tr>
<tr>
<td>Total₁</td>
<td></td>
<td>0.1284</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur added</td>
<td>0.0500</td>
<td>0.0500</td>
<td>0.0365</td>
<td>0.0365</td>
</tr>
<tr>
<td>&quot;poly&quot; sulfur</td>
<td></td>
<td></td>
<td>0.0982</td>
<td>0.0982</td>
</tr>
<tr>
<td>Sulfur in gas trap</td>
<td></td>
<td></td>
<td>0.1784</td>
<td>0.1784</td>
</tr>
<tr>
<td>Total₂</td>
<td></td>
<td>0.1784</td>
<td>0.1783</td>
<td></td>
</tr>
</tbody>
</table>

error = \( \frac{0.1784 - 0.1757}{0.1784} \times 100 = -1.5\% \)
TABLE VI

OXIDATION OF THIOSULFATE TO SULFATE BY IODINE
IN ALKALINE MEDIUM

<table>
<thead>
<tr>
<th>Gram-moles per liter standard Na₂S₂O₃ solution</th>
<th>Gram-moles per liter Na₂S₂O₃ found</th>
<th>Hydroxyl ion concentration, normality</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0999</td>
<td>0.0999</td>
<td>3.69</td>
<td>0</td>
</tr>
<tr>
<td>0.0999</td>
<td>0.1002</td>
<td>3.43</td>
<td>+0.3</td>
</tr>
<tr>
<td>0.0999</td>
<td>0.1004</td>
<td>3.20</td>
<td>+0.5</td>
</tr>
<tr>
<td>0.0999</td>
<td>0.1001</td>
<td>2.77</td>
<td>+0.2</td>
</tr>
<tr>
<td>0.0999</td>
<td>0.1002</td>
<td>2.57</td>
<td>+0.3</td>
</tr>
<tr>
<td>0.0999</td>
<td>0.1000</td>
<td>2.40</td>
<td>+0.1</td>
</tr>
<tr>
<td>0.0999</td>
<td>0.1000</td>
<td>2.00</td>
<td>+0.1</td>
</tr>
<tr>
<td>0.0999</td>
<td>0.1004</td>
<td>1.70</td>
<td>+0.5</td>
</tr>
<tr>
<td>0.0999</td>
<td>0.0998</td>
<td>1.41</td>
<td>-0.1</td>
</tr>
<tr>
<td>0.0999</td>
<td>0.1000</td>
<td>1.33</td>
<td>+0.1</td>
</tr>
<tr>
<td>0.0999</td>
<td>0.0997</td>
<td>1.05</td>
<td>-0.2</td>
</tr>
<tr>
<td>0.0999</td>
<td>0.0991</td>
<td>0.75</td>
<td>-0.8</td>
</tr>
</tbody>
</table>

TABLE VII

DETERMINATION OF SULFITE AND THIOSULFATE IN A
MIXTURE OF THE TWO USING ACIDIC AND ALKALINE IODINE

<table>
<thead>
<tr>
<th>Mixture No.</th>
<th>Constituent</th>
<th>Conc. known g. moles per liter</th>
<th>Conc. found g. moles per liter</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na₂S₂O₃</td>
<td>0.0060</td>
<td>0.0070</td>
<td>+16.70</td>
</tr>
<tr>
<td></td>
<td>Na₂SO₃</td>
<td>0.2265</td>
<td>0.2254</td>
<td>-0.59</td>
</tr>
<tr>
<td>2</td>
<td>Na₂S₂O₃</td>
<td>0.0100</td>
<td>0.0094</td>
<td>-6.00</td>
</tr>
<tr>
<td></td>
<td>Na₂SO₃</td>
<td>0.2370</td>
<td>0.2368</td>
<td>-0.08</td>
</tr>
<tr>
<td>3</td>
<td>Na₂S₂O₃</td>
<td>0.0500</td>
<td>0.0496</td>
<td>-0.80</td>
</tr>
<tr>
<td></td>
<td>Na₂SO₃</td>
<td>0.1716</td>
<td>0.1713</td>
<td>-0.17</td>
</tr>
<tr>
<td>4</td>
<td>Na₂S₂O₃</td>
<td>0.0999</td>
<td>0.0984</td>
<td>-1.50</td>
</tr>
<tr>
<td></td>
<td>Na₂SO₃</td>
<td>0.1117</td>
<td>0.1119</td>
<td>+0.18</td>
</tr>
<tr>
<td>5</td>
<td>Na₂S₂O₃</td>
<td>0.1499</td>
<td>0.1487</td>
<td>-0.80</td>
</tr>
<tr>
<td></td>
<td>Na₂SO₃</td>
<td>0.0559</td>
<td>0.0565</td>
<td>+1.07</td>
</tr>
</tbody>
</table>
**TABLE VIII**

DETERMINATION OF SULFIDE, SULFITE, AND THIOSULFATE IN A MIXTURE OF THE THREE USING ACIDIC AND ALKALINE IODINE

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Conc. known g. moles per liter</th>
<th>Conc. found g. moles per liter</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S₂O₃</td>
<td>0.027</td>
<td>0.026</td>
<td>-3.7</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>0.536</td>
<td>0.534</td>
<td>-0.4</td>
</tr>
<tr>
<td>NaHS</td>
<td>0.209</td>
<td>0.204</td>
<td>-2.4</td>
</tr>
</tbody>
</table>

**TABLE IX**

DETERMINATION OF POLYSULFIDE SULFUR WITH ALKALINE IODINE

<table>
<thead>
<tr>
<th>Constituent</th>
<th>g. moles/liter</th>
<th>S</th>
<th>g. moles/liter</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S</td>
<td>0.2312</td>
<td>0.2312</td>
<td>0.2075</td>
<td>0.2075</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>0.0124</td>
<td>0.0124</td>
<td>0.0004</td>
<td>0.0004</td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>0.0052</td>
<td>0.0104</td>
<td>0.0463</td>
<td>0.0926</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.0028</td>
<td>0.0028</td>
<td>0.0034</td>
<td>0.0034</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>0.2568</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur added</td>
<td>0.1000</td>
<td>0.1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;poly&quot; sulfur</td>
<td></td>
<td>0.3568</td>
<td>0.0574</td>
<td>0.0574</td>
</tr>
<tr>
<td>Sulfur in gas trap</td>
<td></td>
<td></td>
<td>0.0001</td>
<td>0.0001</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>0.3614</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total sulfur (grav.)</td>
<td></td>
<td>0.3568</td>
<td>0.3566</td>
<td></td>
</tr>
</tbody>
</table>

\[
\text{error} = \frac{0.3614 - 0.3568}{0.3568} = +1.3\%
\]
CONCLUSIONS

Chloramine-T is unsuitable for use as an oxidizing agent in the volumetric determination of sulfide and polysulfide sulfur.

The hypohalogenes are suitable for use as standard oxidizing agents in the volumetric determination of sulfide, sulfite, thiosulfate, and polysulfide sulfur where these four substances are present in a solution either alone or in any mixture of the four. Sulfate and carbonate ions may also be present but do not interfere. The maximum accuracy obtainable is about one and one-half per cent of the total sulfur involved.

Of the hypohalogenes, hypoiode (iodine in alkaline medium) is the most convenient to use. When using hypobromite or hypochlorite, iodine must be used also for titrations in acid medium, so three standard solutions are involved in the analysis: sodium thiosulfate, sodium hypochlorite (or hypobromite) and iodine. The use of hypoiode reduces to two the number of standard reagents required for the determination of sulfide, sulfite, thiosulfate, and polysulfide sulfur.

If sulfide, sulfite, and thiosulfate are determined volumetrically, and sulfate is determined gravimetrically, the difference between the sulfur content of these compounds and the total sulfur determined gravimetrically is equal to the polysulfide sulfur content of the solution. This applies only to inorganic liquors. Such an analysis is accurate to within plus or minus two-tenths of one per cent of the sulfur involved.

The strictly volumetric method may be applied to the determination of sulfide, sulfite, thiosulfate, and polysulfide sulfur in an inorganic liquor with fairly accurate results in about two and one-half hours. It is believed that this method is suitable for the purpose of Project 1887.
If very accurate results are desired, then both volumetric and gravimetric methods must be used, and about thirty-six hours are required before the results are at hand.

**FUTURE WORK**

In the corrosion study, the corrosive behavior of the following sodium salts, individually and collectively, will be studied: hydroxide, sulfide, carbonate, bicarbonate, sulfite, sulfate, thiosulfate, polysulfides, and chloride.

The procedures for the determination of these salts individually or in various mixtures is fairly well established, some in this report, and others by long-used and accepted procedures. There is only one case where the accuracy of the determination is in question.

When hydroxyl and carbonate ions are present together in a liquor, in addition to one or more of the basic ions mentioned above, the common practice is to make two acidimetric titrations on the liquor. One titration, termed "total alkali" is made to determine the total neutralization equivalents in the liquor. The other titration, termed "active alkali", is made to determine the neutralization equivalents in the liquor after precipitation of the insoluble barium salts with barium chloride. After addition of barium chloride to a liquor containing any or all of the above mentioned salts, the only anions remaining in solution are chloride, sulfide, and hydroxyl. From a knowledge of the other compounds present determined iodometrically or gravimetrically, and from the results of the two acidimetric titrations, the respective concentrations of carbonate and hydroxyl ion are calculated.

It is the determination termed "active alkali" that is under suspicion. It has been found that it is extremely difficult to obtain checks of closer
than a few tenths of a milliliter of acid used in successive titrations on the same filtrate used for "active alkali". Why this is so, and what the accuracy limits of the method are, is not known. Within the next few weeks some work will be done in the laboratory in an attempt to clarify this situation.

The corrosion study requires that a constant temperature bath be used. This bath, or thermostat, has been designed and the order for its manufacture has been placed.
LITERATURE CITED

12. Ibid. p. 620.
STANDARDIZATION OF SOLUTIONS USED

THIOSULFATE


IODINE

The iodine solutions used were standardized against standard thiosulfate solution.

CHLORAMINE-T, HYPOCHLORITE, AND HYPOBROMITE

Drain from a buret an aliquot of the solution to be standardized into a 250 ml. Erlenmeyer flask, add excess pure potassium iodide, acidify, and titrate the liberated iodine against standard thiosulfate.

SULFITE

Pipet an aliquot of the sulfite solution into a measured excess of acidified standard iodine, and titrate the excess iodine with standard thiosulfate.

SULFIDE

The sulfide solutions used were analyzed for sulfide, sulfite, thiosulfate, sulfate, and total sulfur according to the following procedure:
TRC (Total reducing compounds): Dilute the solution with freshly boiled and cooled distilled water to a concentration about 0.05 normal and fill a 50 ml. buret with the diluted liquor. To a 250 ml. Erlenmeyer flask containing a measured excess of standard iodine and about 10 ml. 20% sulfuric acid, add an aliquot of the diluted solution from the buret in a rapid dropwise manner while swirling the contents of the flask vigorously and constantly. Titrate the excess iodine with standard thiosulfate. The excess iodine should be equal to at least 15 ml. thiosulfate. Perform in duplicate, or triplicate if necessary. Checks should be obtained to within $8 \times 10^{-4}$ equivalents per liter.

SFRC (Sulfide-free reducing compounds): Pipet 25 ml. of the solution into a 250 ml. volumetric flask containing 15-20 ml. glycerine or isopropanol. Prepare a suspension of zinc carbonate from one molar solutions of zinc sulfate and sodium carbonate. The amount of suspension prepared should be in slight excess of that necessary to precipitate the sulfide contained in 25 ml. of the solution. Add the suspension to the solution in the volumetric flask and shake vigorously. Fill the volumetric flask to the mark with freshly boiled distilled water and mix thoroughly. Filter off the precipitate, using quantitative filter paper, a Büchner funnel and a suction flask, until a perfectly clear filtrate is obtained. Two determinations are made on the clear filtrate as follows:

A. Pipet 25 ml. of the filtrate into a measured excess of strongly acidified standard iodine while swirling the iodine. Titrate the excess iodine with standard thiosulfate. Perform in duplicate. Checks should be obtained to within $5 \times 10^{-4}$ equivalents per liter.

B. Pipet 25 ml. of the filtrate into a measured excess of standard Chloramine-T in a 250 ml. glass-stoppered Erlenmeyer flask.
Add sufficient 25% sulfuric acid to give an acid concentration of about 2.5 normal. Stopper the flask and let it stand for about five minutes. Swirl the contents at about one minute intervals. Add excess potassium iodide to the flask and titrate the liberated iodine with standard thiosulfate. Perform in duplicate. Checks should be obtained to within \(1 \times 10^{-3}\) equivalents per liter.

SULFATE

IPC Method 107

TOTAL SULFUR

Pipet 5 ml. of the liquor into a 250 ml. beaker, add 30 ml. 40% hydrogen peroxide and 10 ml. normal sodium hydroxide. Cover with a watch glass and cool with cold water if the reaction becomes too vigorous. Let stand for about eight hours or overnight. Place on a cold hot-plate and, starting with a very low heat, gradually increase the heat until the solution is boiling gently. Boil for about thirty minutes to destroy excess hydrogen peroxide. Add a drop of methyl orange. If the color is discharged hydrogen peroxide is still present and more boiling is required. When all the hydrogen peroxide is destroyed, neutralize with conc. HCl and add 5 ml. excess for every 100 ml. of solution. Precipitate the sulfate with barium chloride in the standard manner, filter, wash, and weigh the ignited precipitate. Perform in triplicate.

Calculations:

\[
\frac{(SFRC-E) - (SFRC-A)}{7} = \text{g. moles/liter thiosulfate}
\]

\[
\frac{(SFRC-A) - (\text{g. moles/liter thio})}{2} = \text{g. moles/liter sulfite}
\]
The calculations for sulfate and total sulfur are commonly used and will not be repeated here.

Iodometric Analysis of a Liquor for Sulfide, Sulfite, Thiosulfate, and Polysulfide Sulfur

TRC-A: Same as TRC for standardization of sulfide solution.

TRC-B: Using a 2 ml. pipet, pipet that amount of the liquor into a 250 ml. beaker. Add 35 ml. 12 normal sodium hydroxide. While the contents of the beaker are being mixed by a magnetic mixer, add standard 0.1 or 0.2 normal iodine at a rapid dropwise rate. The contents of the beaker will, at the start, have a slight yellow tinge. This color will persist while the iodine is being added, but will disappear when the end-point approaches and the solution will be colorless. When the end-point is passed, the contents of the beaker again become yellow, more intensely this time, due to the presence of iodine. When the end-point is reached, note the volume of iodine added, and add 15 to 20 ml. in excess. Dilute the contents of the beaker to about 175 ml. with distilled water, mix, and cool in ice-water. Add 38 ml. conc. (12 N) HCl and titrate the excess iodine with standard thiosulfate. Perform in duplicate. Checks within $8 \times 10^{-4}$ equivalents per liter should be obtained.

SFRC: Precipitate and filter off the sulfide as described in the procedure for standardization of a sulfide solution with the exception that no glycerine or isopropanol may be used. Two determinations are made on the clear filtrate, and these must be completed as rapidly as possible.
A. This determination is the same as described in the procedure for standardization of a sulfide solution.

B. Pipet the 25 ml. aliquot of the filtrate into a 250 ml. Erlenmeyer flask and add 12 ml. 12 normal sodium hydroxide. Titrate with standard iodine, adding the iodine in a steady stream while swirling the contents of the flask. Note the endpoint as described under TRC-B, and add 15 to 20 ml. iodine in excess. Cool in cold water, add 15 ml. conc. (12 N) HCl and titrate the excess iodine with standard thiosulfate. Perform in duplicate. Checks within $8 \times 10^{-4}$ equivalents per liter should be obtained.

Calculations:

Sulfide, sulfite, and thiosulfate are calculated in the same manner as described in the procedure for standardization of a sulfide solution.

Polysulfide sulfur:

Let

- $a =$ sulfide, g. moles/liter
- $b =$ sulfite, g. moles/liter
- $c =$ thiosulfate, g. moles/liter
- $d =$ polysulfide sulfur, g. moles/liter
- $x =$ TRC-B, equivalents per liter

Then

$$d = \frac{x - (8a + 2b + 8c)}{6}$$
A STUDY OF THE CORROSIVE BEHAVIOR OF THE ELECTROLYTES IN ALKALINE PULPING SOLUTIONS

INTRODUCTION

A very brief outline and history of Project 1887 was presented in the Introduction of Project Report No. 1 (Feb. 7, 1956). The major portion of the effort expended on the project up to that time had been devoted to the development of analytical techniques suitable for the determination of the various constituents of alkaline pulping liquors, and no work on corrosion phenomena, as such, had been conducted. Project Report No. 1 reports on the analytical techniques developed and describes briefly a constant temperature bath designed and under construction at that time.

This report gives an account of a literature survey, laboratory experiments on corrosion, and recommendations for future work.
LITERATURE SURVEY

Bibliographies (1), (2), (3) and reviews (4) published in the literature made easy a review of the subject of alkaline digester corrosion. However, the stated objective of this project is to study the corrosive behavior of the electrolytes, individually and collectively, present in alkaline pulping solutions. With few exceptions, and until just recently, the majority of the published papers dealing with digester corrosion view the liquor as an environmental entity and deal little with its composition or the corrosive characteristics of its constituents.

It was felt, therefore, that a search of the literature should be made to determine what is known about the basic corrosive properties of aqueous solutions of the major and minor constituents of alkaline pulping liquors. Those liquor constituents for which bibliographies were made include the sodium salts of carbonate and bicarbonate, sulfate, chloride, sulfite, thiosulfate, sulfide, and hydroxide. Sodium polysulfide was not included because most of the investigations concerning the corrosive properties of this compound are already included in the bibliographies on alkaline digester corrosion. In addition, a number of papers were found in the literature that, while not strictly pertinent to the subject of corrosion, contain subject matter of basic importance to an understanding of the behavior of certain of the compounds of interest in corrosion reactions.

The bibliographies are not necessarily complete in that every paper published on the subject may not be included. An attempt was made to include the major articles published during the period 1915-1954. These bibliographies are included as an appendix to this report.
### TABLE I

**Variables Affecting the Results of a Total Immersion Weight-Loss Test by Influencing or Exerting Their Influence Through Either the Metal Specimen or the Corrosive Environment (Aqueous Solution)**

<table>
<thead>
<tr>
<th>Metal Specimen</th>
<th>Corrosive Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Selection of representative sample of type of metal</td>
<td>1. Purity of chemicals used</td>
</tr>
<tr>
<td>2. Size and shape</td>
<td>2. Concentration of solution</td>
</tr>
<tr>
<td>3. Mechanical preparation of exposed surface</td>
<td>3. Temperature</td>
</tr>
<tr>
<td>4. Physical methods of preparation of exposed surface</td>
<td>4. Ratio of volume of solution to exposed surface area of specimen</td>
</tr>
<tr>
<td>a. Machining</td>
<td>5. Agitation</td>
</tr>
<tr>
<td>b. Cutting (sawing, filing)</td>
<td>6. Aeration</td>
</tr>
<tr>
<td>c. Abrasion (polishing)</td>
<td>7. pH</td>
</tr>
<tr>
<td>5. Chemical methods of preparation of exposed surface</td>
<td></td>
</tr>
</tbody>
</table>
TOTAL IMMERSION WEIGHT-LOSS TESTS

FACTORS AFFECTING REPRODUCIBILITY AND ACCURACY

Up to the present time, weight-loss methods have been primary tools in corrosion studies. A serious drawback of this method has been, and still is, the inconsistency and lack of reproducibility of results obtained through its use. Since some type of weight-loss measurement is indispensable to this proposed study of corrosion, it follows that the weight-loss method itself must be the first object of investigation. The purpose of such an investigation is to identify and examine the variables that affect the consistency and reproducibility of the results. If the weight-loss method of testing is arbitrarily divided into two areas of consideration, viz., (a) the metal specimen, and (b) the corrosive environment, it is then relatively easy to classify the known variables as affecting, or exerting their influence through, either the one or the other. As a result, Table I was compiled for the known and probable variables affecting the results of a total immersion type of test.

Most of the influencing factors listed in Table I will be found in Champion's (5) book on corrosion testing where they are discussed more or less at length, and sometimes in slightly different forms than presented here.

The degree of control exercised over the variables and the attention paid to detail is reflected in the information included in reporting the results of a laboratory total immersion test. The A.S.T.M. (6) recommends that the following information be included in the report of a laboratory total immersion test:
1. The chemical compositions of the metals and alloys tested.

2. The exact size, shape, and area of the specimens.

3. The fabrication and metallurgical history of the specimen.

4. The surface treatment used to prepare specimens for test.

5. The number of specimens of each material tested, whether each specimen was tested in a separate container, or whether specimens were tested in the same container.

6. The chemical composition and volume of the testing solution, and information as to how and to what extent the composition was held constant or how frequently the solution was replaced.

7. The temperature of the testing solution and the maximum variation in temperature during the test.

8. The degree of aeration of the solution in terms of milliliters of air per liter of solution per minute and the maximum variation in this flow, or similar information for the gas or mixture of gases employed.

9. The velocity of relative movement between the test specimens and the solution, and a description of how this movement was effected and controlled.

10. The nature of the apparatus used for the test.

11. The duration of the test or each part of it if made in more than one stage.

12. The method used to clean specimens after exposure and the extent of any error introduced by this treatment.

13. The actual weight losses of the several specimens, depth of pits (plus notes on their size, shape, and distribution, as by sketch), data on mechanical properties before and after if determined, and results of microscopic examination or qualitative bend tests.

14. Corrosion rates for individual specimens calculated in milligrams per square decimeter per day (mdd).

DESIGN OF TEST APPARATUS AND INTERPRETATION OF RESULTS

The design of an apparatus for making weight-loss measurements by the total immersion test is governed mostly by the number of variables it is desired to control and by the degree of control desired. Using Table I and the above information list as an initial guide, the apparatus described later
A quantitative estimation of corrosion in a specific case is made possible by the weight-loss method, but little information is supplied concerning the reaction mechanism of the corrosion process. If one is interested in determining such mechanisms, the weight-loss method alone is insufficient; it should be used in this case as a correlative supplement to other methods of investigation that do give information about corrosion mechanisms.

ELECTROCHEMICAL METHODS

It is almost universally agreed now that the great majority of corrosion processes in aqueous media are electrochemical in nature. It follows, therefore, that suitable electrochemical methods of investigation are best adapted to investigations of reaction mechanisms in corrosion processes. By these means, it is quite often possible to obtain quantitative interpretations of reaction mechanisms, which in turn can be supported by weight-loss measurements.

The electrochemical conventions used in this report, and to be used in subsequent reports, are those adopted by the Electrochemical Society, sometimes referred to as "the European convention." For the purposes of this work, those involved are:

1. anodic currents are counted as negative,
2. the potential of an electrode anodic to a standard saturated calomel reference electrode is given a negative sign,
3. the passive potential range of an electrode is more cathodic (less negative) than the active range, and
4. the current density is defined as the current in milliamperes per square centimeter of apparent electrode surface.
SINGLE ELECTRODE POTENTIALS

If a specimen of the test metal is immersed in an aqueous corrosive environment and coupled with a suitable standard reference electrode through a null-point measuring device, the relative metal-liquid potential difference can be measured. If this potential is measured at the moment of immersion of the metal in the solution and periodic or continuous measurements are made thereafter, a 'potential-time' curve will be obtained. Interpretation of such a potential-time curve gives information about the stability of surface films on the metal in a particular environment. Information may be gained as to whether a metal initially passive, or active in a certain environment, will or will not retain that state; the effect that such variables as temperature, concentration of solution, composition of solution, etc., have on the initial and final states of the metal relative to a specific environment, and, to a limited degree, the type of pretreatment to which the metal was subjected prior to immersion (2). Measurement of single electrode potentials does not give any quantitative data on corrosion phenomena, but does give very useful information on the tendency, or potentiality, of a metal to corrode in a given solution.

Because the potential of a specimen is definitive of its state (active or passive) in a corrosive solution, a very useful aid in the interpretation of weight-loss data would be a system whereby the potential of a specimen immersed for a weight-loss test would be followed during the entire exposure time. This will be discussed further in the experimental section of this report.
POLARIZATION TECHNIQUES

Whereas the measurement of single electrode potentials is a relatively simple matter, the measurement of polarization curves is a little more complicated. Essentially, the method consists of causing, by means of an external e.m.f. such as a storage battery, a current to flow in a cell consisting of the corrosive solution as electrolyte, the metal specimen as either anode or cathode, and another "unpolarizable" electrode. A third electrode is inserted in the cell or connected to it, and electrical connection is made between it and the metal specimen electrode. Most often, this third electrode is a standard reference electrode of some type. The current flowing from the storage battery and between the metal specimen electrode and the unpolarizable electrode is controlled by suitable variable resistances in the line, and is changed either periodically at definite intervals or continuously at a given rate. When the controlled current is changed periodically, the metal specimen electrode-reference electrode e.m.f. is also measured periodically by means of a null-point instrument. If the controlled current is changed continuously at a constant rate, the metal specimen electrode-reference electrode e.m.f. must be measured continuously and simultaneously. The choice of either method of synthesizing polarization curves will depend on the individual views of a given worker. Those who view the variation of overpotential with time as an intrinsic phenomenon of overpotential, will record the constant potential reached after prolonged polarization; those who regard this variation as due to other causes will measure potentials as rapidly as possible with each current change (g).

In either case, a curve is obtained by plotting current density (current per unit area of metal specimen electrode) against the metal specimen electrode potential as measured relative to the reference electrode. From the relative shape and position of anodic and cathodic portions of such curves,
it is possible to identify corrosion stimulators, or "depolarizers," in an aqueous solution. The identification of the polysulfide ion as a cathodic depolarizer in kraft white liquor (9) is a classic example of the type of valuable information that this method of investigation can supply about the mechanism of corrosion processes.

With appropriate modification and refinement of techniques, additional information regarding the mechanism of corrosion processes may be obtained by means of polarization curves: a knowledge of the temperature coefficient will enable one to calculate activation energies for the reactions occurring, equilibrium potentials for irreversible systems can be calculated, transfer coefficients and reaction rates can also be estimated from information obtained from the polarization curve.

If the reactions occurring at the electrodes are known, and one hundred per cent current efficiency is realized, quantitative measure of corrosion rates at various potentials is possible without recourse to gravimetric methods. Under the same conditions, quantitative treatment can also be given to depolarizing reactions occurring at the cathode (7), (10).

The main application of the polarization curve technique in studies of digester corrosion has been as a means of identification of depolarizers in the liquor (7), (9), (10).

OTHER ELECTROCHEMICAL METHODS

Various other electrochemical methods have been used in studies of corrosion mechanisms. Mueller used current density-time curves to measure corrosion rates in both anodic and cathodic regions. Miley used a coulometric
method to determine the thickness of oxide films on iron (11), (12), and copper (13), (14). Price and Thomas used an improvement of Miley's method to identify and measure the thickness of tarnish films on silver, silver alloys, and copper (15). Campbell and Thomas improved Miley's method to study mixed oxide and sulfide films on copper and silver. Lingane (17) used a method of voltammetry at controlled potential to determine the number of electrons involved in an electrode reaction; although this specific application was applied to the electrolytic reduction of picric acid, the method is equally applicable to the anodic dissolution of pure metals as in the case of a specific corrosion reaction.

Other useful electrochemical and electrometric methods of more specific application are outlined in various books (18) and monographs (19).
EXPERIMENTAL

TOTAL IMMERSION WEIGHT-LOSS TESTS

**Constant Temperature Bath**

A constant temperature bath was constructed by Overly's, Inc. sheet metal works of Neenah from a design supplied them by the Institute. Construction was of a double-wall type, with glass wool insulation between the walls. The interior wall was of type 316 stainless steel and exterior surfaces of type 304 stainless steel. Two Pyrex windows were built into opposite sides of the rectangular bath to provide for visual observation of the interior during the course of experiments. The bath was designed to hold about forty gallons of liquid when in operation.

Circulation of the liquid to insure even heat distribution throughout the bath was provided for by means of a type 316 stainless steel Goulds centrifugal pump of twenty g.p.m. capacity against a twenty-foot head. The pump was mounted below the bath proper on an angle iron frame. The suction side of the pump was connected to two outlet ports in diagonally opposite corners on the floor of the bath. A false bottom of three dimensionally equal sections was placed three inches above the floor of the bath. Two of the sections of the false bottom were solid sheet metal, and the third was perforated with three-eighths inch holes at half-inch intervals. The perforated section was placed between the two solid sections to form the false bottom. Thus, the circulating liquid leaving the bath must pass through the center section to reach the outlet ports in the floor. The pressure side of the pump was connected to two inlet ports at diagonally opposite corners near the top of the bath just below the proposed liquid level. Liquid
distributors consisting of perforated stainless steel pipe were fastened to the inner opening of the inlet ports.

Temperature control was obtained by means of electrical immersion heaters and copper cooling coils inserted horizontally in the bath beneath the false bottom. The heating elements consisted of four two-thousand watt electric heaters with stainless steel sheaths; they were arranged in two circuits, each controlled by a separate bimetallic thermoregulator. One circuit was used as an auxiliary unit to assist in reaching the desired temperature with minimum time loss. When the desired temperature was approached within one degree centigrade, this circuit automatically cuts out, leaving the other circuit to carry the temperature rise the remaining distance and to maintain control. This circuit was controlled through relays by a relatively inexpensive Fenwal bimetallic thermoregulator in a stainless steel well built horizontally into the side of the bath at about the midpoint of the liquid depth. The other circuit was used primarily to maintain the temperature desired, and was controlled through relays by an Aminco "Quickset" bimetallic thermoregulator also mounted horizontally in a well in the side of the bath midpoint in the liquid depth. The sensitivity of this regulator is stated by the manufacturer to be ±0.04°C. when used in a horizontal position. The power supply to the two heaters controlled by this sensitive regulator was connected through a variable transformer to provide control over the watt density of the heaters.

Two cooling units consisting of U-shaped one-quarter inch copper tubing connected in parallel to a cold water supply were also inserted beneath the false bottom of the bath. Thus, by proper manipulation of the heaters
and the water coolers, it was made possible to attain constant temperatures as much as ten degrees below ambient.

Tests conducted at temperatures of $35^\circ$, $50^\circ$, $65^\circ$, $80^\circ$, and $95^\circ$C. indicated that, in this temperature range, the constancy of the bath liquid temperature was maintained within $\pm 0.07^\circ$. Ethylene glycol was decided upon as the bath liquid to be used.

**Apparatus and Methods**

The container for the weight-loss measurements was a three-neck, round bottom, one-liter flask. It was placed in the bath so that the whole of the bulb of the flask was immersed, and secured by a clamp around the large central neck. A reflux condenser was fitted into one of the smaller necks through a rubber stopper and the other neck was fitted with a rubber stopper through which passed a three-inch length of six-millimeter Pyrex tubing. Through a sealing gland in the large central neck passed a motor-driven glass stirring rod. Four of the containers just described were placed in the constant temperature bath. Purified nitrogen was passed through the space in the flask above the liquid at a rate of 500 cc./min., using the six-millimeter Pyrex tubing as inlet and the condenser as outlet. The four flasks were so connected that the nitrogen passed through each in series, leaving each flask through the reflux condenser. A cylinder of water-pumped nitrogen was the nitrogen source, and the gas was purified ($O_2$ removed) by passing it over copper turnings at $450^\circ$C. followed by washing in alkaline pyrogallol. A gas flowmeter was installed following the purification train.

The solutions were made from C. P. salts in boiled distilled water stripped of dissolved oxygen and carbon dioxide by bubbling through it
purified nitrogen. The solutions, once made up, were stored under a pressure of about one half inch of mercury. When solution was withdrawn from the storage bottle, the volume removed was continuously replaced by purified nitrogen. When the test containers were filled with the solution, they were first flushed of air with purified nitrogen, and while the solution was entering the containers, purified nitrogen was also passed through the container and out past the entering stream of solution. Each container was filled with about 750 ml. of the solution for each test.

The steel samples used for the weight-loss tests were of A-285 low silicon steel obtained from A. O. Smith Corporation of Milwaukee. The material was cut from one-half inch plate stock U.S.S. heat 547483-8-4 having the following chemical analysis and physical properties:

<table>
<thead>
<tr>
<th>Material</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.19%</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.43%</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.009%</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.030%</td>
</tr>
<tr>
<td>Tensile</td>
<td>61900 p.s.i.</td>
</tr>
<tr>
<td>Yield</td>
<td>38780 p.s.i.</td>
</tr>
<tr>
<td>Elong. 8 in.</td>
<td>28%</td>
</tr>
</tbody>
</table>

Cylindrical samples 2.55 cm. long and 0.32 cm. in diameter were turned from the steel and degreased in a Soxhlet extraction apparatus using an alcohol-benzene azeotrope. Upon removal from the Soxhlet apparatus, each sample was rubbed with moist powdered pumice on a cheesecloth to produce a standard surface finish. The samples were then dried with a soft cloth, rinsed in pure acetone, and stored in a desiccator above calcium chloride. Porcelain combustion boats were used for weighing the samples on an analytical
balance. Weighings were made to the nearest tenth of a milligram.

For removal of corrosion products from the surface of the sample upon termination of a test, the following standard procedure was adopted:

1. Upon removal of the sample from the test solution, rinse it immediately in distilled water, and then place it in absolute alcohol while removing the others.

2. Remove the sample from the alcohol and remove any loosely adhering corrosion products by rubbing it with a paper towel.

3. Remove tightly adhering corrosion products by rubbing with moist pumice powder and a damp cheesecloth.

4. Rinse the sample in distilled water and acetone in that order.

5. Place the sample in a desiccator for two hours before weighing.

As indicated in the Data section of this report, two periods of exposure were used in the weight-loss experiments, a twenty-four hour period and a forty-eight hour period. When the period of exposure was lengthened to forty-eight hours, a few changes in the apparatus were also made. This consisted essentially of removing the glass stirring rod and motor used for agitation, and using a substitute method of agitation which consisted of lengthening the nitrogen inlet tube so that it extended to within an inch and a half of the bottom of the flask, moving the tube to the large central neck, and bubbling the nitrogen through the solution. This left one of the small necks free for entry and removal of the samples.

The cylindrical samples were dropped into the flask at the beginning of a test and removed by means of a small Teflon-covered Alnico magnet at the end of the test. The sample was adjusted to rest horizontally in the flask,
supported at a point at each end against the curved wall of the flask.

ELECTROCHEMICAL TESTS

Single Electrode Potentials

The potential measurements were made on samples of the same steel used for the weight-loss measurements. All potentials were measured relative to a standard calomel reference electrode, using a saturated potassium chloride solution in the built-in salt bridge; specifically, the type used was a Beckman 8970-13 reference electrode, which has a temperature range from 0-100°C. in continuous use. The calomel electrode was immersed in the same solution as the steel sample; therefore, the electrode was at the same temperature as the steel. This eliminates temperature corrections as are necessary when the reference electrode is external to the test vessel and connected to it by means of a salt bridge.

Two instruments were used for making the potential measurements, a Beckman model H-2 pH meter and a student potentiometer. The pH meter was used as a rapid indicating device when the rate of change of potential was too rapid to follow with the manually balanced student potentiometer. Using the student potentiometer as a standard, the readings obtained by the pH meter were occasionally checked. Generally, the two instruments gave measurements identical to the millivolt, but occasionally a difference of a few millivolts was noted. This is well within the degree of precision required for measuring single electrode potentials for the purposes of this study.

Electrode potentials are best measured by completely immersing the electrode in the electrolyte, yet there must be a means of electrical connection that will not affect the measurements or be affected by the electrolyte.
This problem was met by designing the type of electrode shown in Figure 1. A Teflon rod four and one-quarter inches long by seven-sixteenths inch in diameter was threaded internally at one end to a depth of about three-eighths of an inch; a five thirty-seconds inch hole was drilled the remainder of the length of the rod through its center. A steel electrode was made which could be screwed into the threaded end of the Teflon rod so that the sides and one end of a disk thirteen sixty-fourths inch in diameter and one-sixteenth inch thick was exposed to the solution. Electrical connection was made by inserting a one-eighth inch mild steel rod threaded at one end through the hole in the Teflon rod and screwing it into the internally threaded portion of the steel electrode. A tight seal between the shoulder of the steel electrode and the end of the Teflon rod was effected by means of a gasket made of dental dam. When the electrode was tightened into the Teflon rod, the squeezed-out edges of the gasket were trimmed with a razor blade.

A sketch of the arrangement for measuring single electrode potentials is presented in Figure 2. A three-neck, one-liter, round-bottom flask was immersed in a small thermostat which controlled temperature to within ±0.05°C. The same technique for making and storing solutions, and filling the flask described previously for the weight-loss tests was used here. Slight agitation of the solution was obtained by bubbling purified nitrogen through the solution at a rate of about four hundred milliliters per minute. The nitrogen left the container through a reflux condenser.

The potential measurements were made at temperatures of 35, 65, and 90°C. to determine the temperature effect on the initial and final
Figure 1. Steel electrode used for potential-time measurements.
Figure 2. Apparatus used for making single electrode potential measurements.
states of the steel electrodes and on the potential-time curve as a whole. Two initial states were chosen for the steel samples: the active state, which was produced by scrubbing the steel with moist pumice powder followed by immersion in normal hydrochloric acid until hydrogen was continuously evolved, and a slightly passivated state which was produced by allowing the steel samples to remain in the desiccator for two to four days after the degreasing and cleaning procedure. The active electrodes were removed from the acid, rinsed in distilled water, and immersed in the solution with as little exposure to the air as possible. The slightly passivated electrodes were removed from the desiccator and immersed immediately in the solution. In either case the initial potential reading was made as quickly as possible (within a few seconds) after the samples were immersed, and periodic measurements were made thereafter until it was evident that the potential had reached a final stable state. In some cases the experiment was terminated before an apparently stable state had been attained, but the rate of change of potential was so slow that continued measurements would serve only to prolong the experiment.

Corrosion-Potential Measurements

A few short-time weight-loss measurements were made in kraft white liquor while the potential of the sample was checked occasionally. The sample used for these experiments was ASTM A-285 low-silicon partially rimmed steel obtained from A. O. Smith in sheets 2 by 7 by 1/16 inches. The metal was from U.S.S. heat no. 569743-10-2 having the following A. O. Smith check analysis:

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.17%</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.53%</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.12%</td>
</tr>
</tbody>
</table>
Sulfur 0.020%
Silica low

The steel was received in the hot rolled condition. Strips 0.14 cm. thick by 0.54 cm. wide by 8.14 cm. long were machined from the large samples and the surface was freshened by abrasion with fine emery cloth. The strips were then degreased as previously described and stored in a desiccator. Active samples were prepared by immersion in HCl as before and passive samples were prepared by allowing them to remain in the desiccator after activation in HCl, rinsing in distilled water and drying with a paper towel for a specified time. The samples were immersed in the liquor except for about a quarter inch at the top to which was fastened a small alligator clip for electrical connection. This gave an exposed area of 10.3 sq. cm. The samples were cleaned of corrosion products by rinsing in distilled water, rubbing off the loose products with a paper towel and dissolving off the tightly adhering portion in \(0.1N\) HCl. Weighings were made on an analytical balance to the nearest tenth of a milligram.

Measurements were made in both oxygen-free kraft white liquor and in liquor open to the air. The oxygen-free liquor was made and stored in the manner previously described for the solutions used in the weight-loss tests. The concentration of the liquor was the same in both cases: 35 g./l. Na\(_2\)S and 100 g./l. NaOH. The liquors were not analyzed.

**Polarization Experiments**

Only a few polarization experiments were performed, and these were only of an exploratory nature, the major purpose of which was to familiarize the author with the experimental techniques involved. Further polarization experiments were deferred until suitable instrumentation became available.
The steel electrode used for the potential-time measurements was also used for the polarization experiments. The main advantage in using such a type of electrode is that the apparent surface area is exactly defined, thus facilitating the calculation of current densities. The experimental arrangement used for making polarization studies was essentially the same as that used for measuring single electrode potentials with the exception of the electrical arrangement. A diagram of the measuring and polarization circuits is presented in Figure 3.

The polarization experiments were carried out in stirred kraft white liquor 35 g./l. Na₂S and 100 g./l. NaOH at room temperature. No attempt was made to keep the liquor from contact with the air. The liquor was not analyzed.

The auxiliary electrode consisted of a square inch of platinum foil fused to a coiled platinum wire 0.032 inches in diameter. The surface area of the auxiliary electrode was 17.3 square centimeters. The auxiliary electrode was placed in a separate compartment connected to the main body of the liquor in the electrolysis cell by means of a fritted glass disk of "fine" porosity. This compartment was immersed in the main body of the liquor in the cell. A sketch of the auxiliary electrode and its compartment is presented in Figure 4.

The procedure used in the polarization experiments was as follows: The steel electrode was connected as cathode to the polarization circuit, the auxiliary electrode as anode, and both were immersed in the kraft white liquor in the electrolysis cell. The applied e.m.f. was adjusted by means of R₁ and R₂ until the ammeter needle rested exactly on zero. R₁ was
Figure 4. Auxiliary electrode used in polarization experiments.
adjusted and set so that the maximum setting of $R_2$ corresponded to a full-scale reading of the milliammeter. The electrodes were kept in the white liquor with no current flowing for about twenty minutes, during which the e.m.f. across $e_2-e_3$ was measured periodically. When this e.m.f. became fairly stable, polarization of $e_2$ was begun. $R_2$ was adjusted so as to allow a small current to pass between $e_2$ and $e_1$. While this small current was flowing, the e.m.f. across $e_2-e_3$ was measured. When this e.m.f. became fairly stable, the reading was recorded with the corresponding current reading, and $R_2$ was adjusted so that a slightly larger current flowed. The applied e.m.f. was indicated by the voltmeter $V$. By repeating this procedure, a number a current-potential points were obtained until the potential of hydrogen evolution was approached. When the peak applied e.m.f. was reached, the current potential relationship obtained by decreasing the applied e.m.f. was also recorded by reversing the procedure.
DATA AND RESULTS

WEIGHT-LOSS TESTS

The weight-loss data obtained thus far are presented in tabular form in Tables II and III. They are illustrated graphically in Figures 5, 6, and 7.

Table II and Figure 5 represent the initial experiments made in conducting weight-loss tests. They were obtained using duplicate specimens in separate containers for twenty-four hours' exposure. The conditions of exposure were described in the Experimental section of this report.

Table III and Figures 6 and 7 represent weight-loss data obtained for forty-eight hour exposure periods on quadruplicate specimens in separate containers. As indicated in the Experimental section of this report, a few minor changes were also made in the conditions of exposure.

SINGLE ELECTRODE POTENTIALS

Potential-time curves for steel in oxygen-free solutions of several of the electrolytes of interest are presented in Figures 5 through 20. The method and apparatus used was described in the Experimental section of this report.

CORROSION-POTENTIAL MEASUREMENTS

The data for corrosion-potential measurements described in the Experimental section are presented in Tables IV and V. The initial potential was measured as quickly as possible after immersion of the steel in the liquor.
TABLE II

WEIGHT-LOSS DATA FOR DUPLICATE SPECIMENS IN OXYGEN-FREE AQUEOUS SODIUM SULFATE AND SODIUM CHLORIDE; 24-HOUR EXPOSURE, SOLUTION MECHANICALLY STIRRED (SPECIMEN SURFACE AREA 0.0272 SQ. DM.)

<table>
<thead>
<tr>
<th>Temp., °C.</th>
<th>Sodium Sulfate(^1)</th>
<th>Sodium Chloride(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>0.5</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>29.4</td>
</tr>
<tr>
<td>50</td>
<td>1.1</td>
<td>40.5</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>36.8</td>
</tr>
<tr>
<td>65</td>
<td>0.8</td>
<td>29.4</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>18.3</td>
</tr>
<tr>
<td>80</td>
<td>1.1</td>
<td>40.5</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>25.7</td>
</tr>
</tbody>
</table>

\(^1\) 0.0111 g.-mole/liter, pH = 5.39 at 25°C.

\(^2\) 0.0024 g.-mole/liter, pH = 5.61 at 25°C.
TABLE III

WEIGHT-LOSS DATA FOR QUADRUPLICATE SPECIMENS IN OXYGEN-FREE AQUEOUS SODIUM SULFATE AND SODIUM ACETATE; 48-HOUR EXPOSURE, SOLUTION AGITATED BY BUBBLING NITROGEN
(SPECIMEN SURFACE AREA 0.0272 SQ. DM.)

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>Sodium Sulfate¹ Weight-loss, mg.</th>
<th>Corrosion rate, mdd.</th>
<th>Sodium Chloride² Weight-loss, mg.</th>
<th>Corrosion rate, mdd.</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>0.6</td>
<td>22.0</td>
<td>0.1</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>22.0</td>
<td>0.2</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>18.3</td>
<td>0.2</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>7.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>50</td>
<td>0.8</td>
<td>29.4</td>
<td>0.4</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>29.4</td>
<td>0.5</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>22.0</td>
<td>0.5</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>18.3</td>
<td>0.5</td>
<td>18.3</td>
</tr>
<tr>
<td>65</td>
<td>0.9</td>
<td>33.1</td>
<td>0.4</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>29.4</td>
<td>0.7</td>
<td>25.7</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>22.0</td>
<td>0.4</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>22.0</td>
<td>0.4</td>
<td>14.7</td>
</tr>
<tr>
<td>80</td>
<td>0.7</td>
<td>25.7</td>
<td>0.5</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>36.8</td>
<td>0.2</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>29.4</td>
<td>0.3</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>36.8</td>
<td>0.3</td>
<td>11.0</td>
</tr>
<tr>
<td>95</td>
<td>0.7</td>
<td>25.7</td>
<td>0.5</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>47.7</td>
<td>0.9</td>
<td>33.1</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>29.4</td>
<td>1.2</td>
<td>44.1</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>25.7</td>
<td>1.2</td>
<td>44.1</td>
</tr>
</tbody>
</table>

¹ 0.0100 g.-mole/liter, pH = 5.17 at 25°C.

² 0.0555 g.-mole/liter, pH = 8.30 at 25°C.
Figure 5. Corrosion rates of mild steel in O₂-free NaCl and Na₂SO₄, 24-hour exposure.
Figure 6. Corrosion rate of mild steel in O₂-free Na₂SO₄, 48-hour exposure.
Figure 7: Corrosion rate of mild steel in O₂-free sodium acetate, 48-hour exposure.
Figure 8. Potential-time relationship of steel in O₂-free white liquor at 35° C.

(100 g/l NaOH, 35 g/l Na₂S).

- O STEEL ACTIVATED
- • STEEL SLIGHTLY PASSIVATED

TIME, MINUTES

E, VOLTS
Figure 9. Potential-time relationship of steel in O₂-free white liquor at 50°C.
(100 g./l. NaOH, 35 g./l. Na₂S).
Figure 10. Potential-time relationship of steel in O₂-free sodium chloride solution (2.4 x 10⁻³ molar).
Figure 12. Potential-time relationship of steel in O₂-free sodium sulfate solution (1.11 x 10⁻² molar).

- O 35°C, STEEL ACTIVATED
- 65°C, STEEL ACTIVATED
- 95°C, STEEL ACTIVATED

Time, Minutes

E', Volts
Figure 13. Potential-time relationship of steel in O₂-free sodium thiosulfate solution (5.2 x 10⁻³ molar).
Figure 14. Potential-time relationship of steel in O₂-free sodium thiosulfate solution (5.2 x 10⁻³ molar).
Figure 15. Potential-time relationship of steel in O₂-free sodium thiosulfate solution at 90°C. \((4.33 \times 10^{-2}\) molar).
Figure 16. Potential-time relationship of steel in O$_2$-free sodium sulfite solution (0.5 molar).
Figure 17. Potential-time relationship at 90°C of steel in O₂-free 0.5 molar sodium sulfite containing 0.04 mole/liter sodium thiosulfate.
Figure 18. Potential-time relationship of steel in O₂-free sodium hydroxide solution (0.3 molar) at 35°C.
Figure 10. Potential-time relationship of steel in O₂-free sodium acetate solution (5.5 x 10⁻³ molar).
Figure 20. Potential-time relationship of steel in O₂-free sodium acetate solution (5.5 x 10⁻² molar).
### TABLE IV

**CORROSION-POTENTIAL EXPERIMENTS IN O₂-FREE WHITE LIQUOR**

#### 35°C.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.880</td>
<td>-1.132</td>
<td>-1.144</td>
<td>0.4</td>
<td>37.2</td>
<td>0</td>
</tr>
<tr>
<td>-0.730</td>
<td>-0.830</td>
<td>-1.144</td>
<td>0.5</td>
<td>46.6</td>
<td>19</td>
</tr>
<tr>
<td>-0.690</td>
<td>-0.828</td>
<td>-1.142</td>
<td>0.6</td>
<td>55.8</td>
<td>42</td>
</tr>
<tr>
<td>-0.690</td>
<td>-0.813</td>
<td>-1.143</td>
<td>0.7</td>
<td>65.2</td>
<td>71</td>
</tr>
<tr>
<td>-0.670</td>
<td>-0.770</td>
<td>-1.136</td>
<td>0.7</td>
<td>65.2</td>
<td>166</td>
</tr>
</tbody>
</table>

#### 50°C.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.100</td>
<td>-1.145</td>
<td>-1.149</td>
<td>0.8</td>
<td>74.6</td>
<td>0</td>
</tr>
<tr>
<td>-0.760</td>
<td>-1.125</td>
<td>-1.152</td>
<td>0.6</td>
<td>55.8</td>
<td>21</td>
</tr>
<tr>
<td>-0.850</td>
<td>-1.135</td>
<td>-1.156</td>
<td>0.5</td>
<td>46.6</td>
<td>42</td>
</tr>
<tr>
<td>-0.850</td>
<td>-1.130</td>
<td>-1.154</td>
<td>0.6</td>
<td>55.8</td>
<td>69</td>
</tr>
<tr>
<td>-0.720</td>
<td>-1.095</td>
<td>-1.152</td>
<td>0.6</td>
<td>55.8</td>
<td>192</td>
</tr>
</tbody>
</table>

### TABLE V

**CORROSION-POTENTIAL EXPERIMENTS AT 50°C. IN WHITE LIQUOR OPEN TO THE ATMOSPHERE**

#### 50°C.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.070</td>
<td>-1.100</td>
<td>-1.090</td>
<td>1.0</td>
<td>93.2</td>
<td>0</td>
</tr>
<tr>
<td>-0.730</td>
<td>-1.070</td>
<td>-1.085</td>
<td>0.9</td>
<td>83.8</td>
<td>21.5</td>
</tr>
</tbody>
</table>
Figure 21. Cathodic polarization of steel in white liquor.
Figure 22. Complete polarization curve of steel in white liquor.

- Mueller's Data
- Author's Data

CURRENT DENSITY, MA/CM²

E VOLTS
The "30-second potential" was measured exactly thirty seconds after the initial reading was obtained. The final potential was measured just before removing the steel from the liquor. In all cases the exposure time was two and one-half hours.

POLARIZATION EXPERIMENTS

A typical cathodic polarization curve is presented in Figure 21. As indicated, two sets of data were obtained, one with increasing applied e.m.f., and the other with decreasing applied e.m.f.

Figure 22 is a complete polarization curve in which the cathodic portion was drawn from the curve obtained with decreasing applied e.m.f. in Figure 21, and the anodic portion was drawn by re-plotting a typical anodic curve obtained by Mueller (19) by decreasing applied e.m.f. This complete polarization curve is presented here mainly as an assurance that the exploratory data obtained by the author is consistent with that obtained by other workers in this field who may also be more experienced. Inconsistency would be indicated by failure of the two sets of data to form a continuous curve by junction at current density zero, assuming closely similar conditions.
DISCUSSION OF DATA AND RESULTS

WEIGHT-LOSS TESTS

The weight-loss tests conducted thus far were made in the absence of oxygen in solutions of sodium chloride, sulfate, and acetate. The concentrations of the solutions were determined by the concentration at which these salts usually appear in alkaline pulping liquors, with the exception of sodium acetate, which is found in neutral sulfite spent liquor. Sodium acetate is included in this initial study mostly because no data was found in the literature about its corrosive action on mild steel.

As indicated in the Appendix, there is much data in the literature on the corrosive power of aqueous sodium chloride and sodium sulfate solutions. In spite of this, very little quantitative data is available that pertains to the conditions obtaining in this work. Therefore, the available information on these two salts is useful mainly as a qualitative guide in interpreting the results obtained in this work.

As can be seen in Tables II and III, the actual loss in weight of any given specimen was very low, generally below one milligram. The weighing accuracy was only one tenth of a milligram. Under these conditions, very little can be concluded as regards the reproducibility or accuracy of the results. It was for this reason that the exposure time was doubled from twenty-four hours to forty-eight hours.

That a corresponding increase in corrosion rate was not obtained by doubling the exposure time is evident from a comparison of Figure 6 with the
sodium sulfate curve in Figure 5. In fact, the corrosion rate cannot be said to have increased at all. This is in agreement with indications that iron and steel become passive in sodium sulfate solutions (20, 21, 22, 23, 24).

The weight loss of the specimens in sodium sulfate represents, then, the amount of metal dissolved while the protective film was forming. This interpretation can be corroborated by continuously measuring the single electrode potential of an active specimen exposed to the test conditions and noting the time required for the potential to reach the passive range. Figure 12 shows the behavior of such a sample in the same solution in which the weight-loss tests were conducted. The potential of the electrode was measured for only an hour, but, except at 90°C., there appears to be a tendency for the electrode potential to drift toward a more positive (passive) value. This trend is not shown by specimens initially slightly passive and exposed under the same conditions (Figure 11). One interpretation of this finding might be that the thin air-formed film is unstable in the corrosive solution and is destroyed by it; a new, and different, film is then built up by reaction of the steel electrode with the sulfate solution. Thus, a longer period of time would be required for these two reactions to take place than would be required when there is no air-formed film to be destroyed (Figure 12).

The upper curve in Figure 5 shows the corrosion rate of steel in a dilute sodium chloride solution. As would be expected on a comparative basis, the corrosion rate in sodium chloride is greater than in sodium sulfate. Again the loss in weight of the samples was very low for the twenty-four hour exposure test. No forty-eight hour exposure test was made in sodium chloride solution.
Figure 10 shows the potential-time relationship of steel in the same sodium chloride solution that was used for the weight-loss tests. A surprising result of the potential measurement is that at thirty-five degrees centigrade an initially active sample quickly becomes passive and a slightly passivated sample retains that state. No indication that this could happen to steel was found in the literature, although this may happen in the case of cast iron (25, 26).

Figure 7 shows the corrosion-rate vs. temperature for steel in sodium acetate, 0.05 molar. Although this salt cannot be properly included in a study of the electrolytes in alkaline cooking liquors, its occurrence in appreciable quantities in neutral sulfite spent liquors prompted much interest in its corrosive properties. The only useful corrosion data on sodium acetate found in the literature was a polarization study by Masing (27). A translation of his paper has not yet been obtained, and the English abstract is extremely brief.

Table III shows that the losses in weight of steel specimens in a sodium acetate solution for twenty-four hours are very small, and this is, of course, reflected in Figure 7. Figures 19 and 20 show the potential-time relationship of steel in the same solution. In Figure 19, the arrests of the curves between -0.5 and -0.6 volts shows a tendency of a specimen initially slightly passive to try to retain that state, while activated samples (Figure 20) show no indication of becoming passive during the time that the potential measurements were made. An interesting result of the measurement of single electrode potentials in sodium acetate solution is the relatively large temperature effect as shown by the distance between the flat portions.
of the curves in Figures 19 and 20.

Perhaps the most striking result of the weight-loss tests is the apparent decrease in corrosion rate at some temperature above fifty degrees. In chloride and sulfate solutions, this occurs at $65^\circ$ for both periods of exposure. In acetate solutions, this decrease occurs at $80^\circ$. One possible explanation is that this decrease is not a true one, but is caused by the lack of sensitivity and accuracy of the test method itself. While the experimental error is undoubtedly included in the results, it does not seem probable that this error would occur so consistently and be so pronounced at one temperature for the number of specimens subjected to exposure both for twenty-four hours and for forty-eight hours. The exception is sodium acetate, where the decrease occurs at $80^\circ$. Instead of a sharp decrease in corrosion rate as occurs at $65^\circ$ in Figure 5, a more accurate picture of the corrosion rate vs. temperature relationship is probably shown in Figure 6 where there is a leveling off of corrosion rate.

SINGLE ELECTRODE POTENTIALS

The primary use of single electrode potential measurements in this report is as an aid in the interpretation of weight-loss test results. In future polarization studies these measurements will have added value in determining the depolarizing characteristics of the same salts in alkaline liquors.

Figures 8 and 9 show potential-time curves of steel in kraft white liquor in the absence of oxygen at $35^\circ$ and $50^\circ$C, respectively. These two figures are representative of many potential-time curves made in white liquor in which the initial condition of the steel sample was varied to determine
the effect of this variance on the ultimate state reached by the steel in the liquor.

Mueller (7) studied extensively the effect of specimen pretreatment on the potential-time relationship of the specimen in kraft white liquor and found that very minor differences in the pretreatment affect very drastically the final state (active or passive) attained by the specimen. He made no attempt to eliminate atmospheric oxygen as a variable in his studies, and found that the type of pretreatment determined whether the specimen became passive in the potential range -0.65 to -0.80 volts or active in the potential range -1.05 to -1.10 volts. Mueller's experiments were carried out at room temperature with no attempt at temperature control.

Figures 8 and 9 are representative of ten potential time curves made on steel in white liquor at 35° and 50°C. in which the final act of preparation of the specimen was activation in hydrochloric acid followed by rinsing in distilled water and drying with a paper towel. Those samples that were not immediately immersed in the liquor were placed in a desiccator, and a single sample was removed and tested as time went on. The time in the desiccator was taken as a rough indication of the degree of passivity that any given sample would exhibit. At definite periods up to 192 hours, the specimens were removed from the desiccator and tested. A few of the specimens exhibited a slight arrest in their potential-time curve, such as the lower curve in Figure 8, but none reached the passive state as their final state. In fact, they all very quickly became active at a very narrow potential range between -1.125 and 1.150 volts in contrast to the wide potential range described by Mueller (7). Also the active active range of potentials observed in this work were consistently lower by -0.05 volts below the lower limit of the active range observed by Mueller (7).
The fact that none of the specimens became passive at either temperature, even after eight days in the desiccator, indicates (a) that steel specimens prepared for weight-loss tests in kraft white liquor may be considered to be in the active state (after undergoing the preparation procedure described earlier) even after storage in a desiccator for over a week; thus the step of activating the samples in HCl after weighing and immediately prior to immersion may be eliminated. This rules out one possible source of error in the weight-loss tests in kraft white liquor: loss of metal by dissolution in the HCl used to activate the specimen, (b) Oxygen may have some effect on the formation of a protective film on steel in kraft white liquor. This seems to be in opposition to Mueller's most recent paper (10) in which it is concluded that the effect of oxygen is limited to producing sulfur compounds in intermediate stages of oxidation, which in turn act as cathodic depolarizers (corrosion stimulators).

That the observed potential range in the active state is lower than that observed by Mueller (7) is in agreement by analogy with Pourbaix's (28) experience that the absence of oxygen in sodium hydroxide solutions decreases the potential of the specimen.

Figures 13 and 14 show the potential-time relationships of steel in sodium thiosulfate, $5.2 \times 10^{-3}$ molar. Despite the variation in specimen pretreatment and in the temperature of the solution, all of the six specimens very quickly reached and maintained an active state close to -0.8 volts. When the specimens were removed from the solution at the end of the test, all were covered with a dense velvety-black coating which dissolved very rapidly and completely in dilute hydrochloric acid with the formation of
gas bubbles. This gas was quickly identified by its odor as hydrogen sulfide. Therefore, the black coating was obviously an iron sulfide. In view of these interesting results, the next series of potential-time measurements were made on steel electrodes in a sodium thiosulfate solution about eight times stronger.

Figure 15 shows the results obtained in a thiosulfate solution 4.33 $\times$ $10^{-2}$ molar at 90°C. At 35° and 65°, the specimens also quickly became active in this solution, but are not shown in Figure 15 because they would only obscure each other. The same black coating was formed which liberated hydrogen sulfide upon dissolution in hydrochloric acid. An effect of the increased concentration of thiosulfate is reflected in the downward slope of the curve in Figure 15. This may be interpreted as follows: Due to a greater concentration of thiosulfate, the black film is formed more quickly and reaches a thickness sufficient to slow down the reaction between the metal electrode and the thiosulfate in a shorter time than in the more dilute solution. Therefore the potential of the electrode steadily drifts toward more positive (passive) values as the film thickness increases.

It is well known that, in acid solution, thiosulfate decomposes to form elemental sulfur and bisulfite (29).

$$S_2O_3^- + H^+ = HSO_3^- + S$$

(1)

and that elemental sulfur in its different forms reacts with iron to form iron sulfide (9, 30, 31).

$$Fe + S = FeS$$

(2)

The pH of the more dilute thiosulfate solution was 6.65 at 25°C and that of the more concentrated was 6.15 at 25°C. Therefore the conditions were favorable for Reaction (1) to take place, and Reaction (2) would follow. Thus the attack of steel by a pure oxygen-free solution of sodium thiosulfate may
The action of thiosulfate upon mild steel in strongly alkaline solutions such as kraft white liquor has been rather satisfactorily explored \((7, 9, 10)\) but little is known concerning its corrosive properties in more mildly alkaline solutions such as neutral sulfite cooking liquor. As a step in this direction, potential time curves were made in pure sodium sulfite solution and in sodium sulfite solution containing sodium thiosulfate.

Figure 16 shows the potential-time relationship of a steel electrode in an oxygen-free 0.5 molar sodium sulfite solution. The specimen initially slightly passive at \(35^\circ\) retained its passive state and reached a stable potential slightly below -0.4 volts. Even at \(65^\circ\), the sample showed some reluctance to becoming active, requiring about fifteen minutes to reach the active state at about -0.85 volts and showing two arrests, one at about -0.55 volts and another at -0.75 volts. At \(90^\circ\), the specimen became active in a few minutes. None of the specimens initially active became passive during the period of test. In almost all cases where the specimen reached the active state, there was a subsequent downward slope of the potential-time curve, indicating a tendency to return to the passive state. This was also observed in sodium thiosulfate solution as shown in Figure 15. This slow drift of the potential of an active specimen toward more positive (passive) potentials is best explained by Evans \((32)\): "It is generally agreed that an originally active anode will not become passive until the liquid in contact with it has become saturated with the anodic product, since only then can an obstructive crust appear upon the metallic surface." The time for passivation to set in then would depend upon the volume of the solution and the solubility, in that solution, of the corrosion product. Since ferrous sulfite is only very slightly soluble in water \((33)\), it may be predicted that steel in sodium sulfite will become passive in relatively short periods of time. In addition,
sodium sulfite is a rather well known corrosion inhibitor (34, 35, 36, 37).

Figure 17 shows the potential-time relationship of steel in oxygen-free 0.5 molar sodium sulfite to which had been added 0.04 mole per liter of sodium thiosulfate. The only temperature at which the measurements were made was 90°. In contrast to a pure solution of either thiosulfate (Figure 15) or sulfite (Figure 16), a specimen initially slightly passive and immersed in the solution at 90° did not become active, but finally approached the passive state near -0.4 volts. However, no black coating was observed on the electrode surface as was the case in a pure thiosulfate solution. An initially activated sample behaved much the same as that type of sample did in pure thiosulfate and pure sulfite solutions. The cause of these results can be examined by suitable polarization experiments in the future.

Figure 18 shows the strongly passivating action of oxygen-free sodium hydroxide upon mild steel. Several more potential-time curves were made in sodium hydroxide solution, but only those three in Figure 18 are presented as representative of the curves obtained. Pourbaix (28) and others (38, 39) have found that sodium hydroxide is an effective inhibitor of steel corrosion.

CORROSION-POTENTIAL MEASUREMENTS

By making weight-loss measurements on steel specimens while their potentials were measured, it was originally intended that a correlation could be obtained between the corrosion rate and the potential of the specimen. However, no clear pattern has yet shown itself from the few experiments made thus far, as is evident from an examination of Table IV. Due to the short (2-1/2 hr.) exposure time, the losses in weight of the specimens were too small to be accorded any degree of accuracy. Because all of the speci-
mens rather quickly became active, the difference in their corrosion rates is too small to be significant.

An interesting result of the corrosion potential measurements may be seen by comparing the final potential of the specimens in the absence of oxygen (Table IV) with the final potential in the presence of oxygen (Table V). It is also evident that the corrosion rates are different. The final potential attained by the steel specimens in white liquor at 50°C, open to the atmosphere falls in the active potential range -1.05 to -1.10 volts described by Mueller (7) and commented upon earlier in this report, but when oxygen is excluded, the final potential reached is more negative by about -0.05 volts at both 35°C and 50°C, and the corrosion rate definitely is less than when oxygen is not excluded.

These results, and the apparent contradiction to Mueller's (10) statement of the effect of oxygen in kraft digester corrosion mentioned previously, are in fact explained very well by his theory. If corrosion of steel in white liquor is electrochemical in nature, the presence of depolarizers is essential for the flow of a corrosion current between anodic and cathodic areas of the steel. Further, if these depolarizers are sulfur compounds in intermediate stages of oxidation, or depend upon these sulfur compounds for their continued existence, then it is necessary to have some oxidizing agent present to continuously replenish the supply of these depolarizers as they are used up in the corrosion process. The only oxidizing agent available to carry out this function in kraft white liquor is oxygen itself, from the atmosphere.

This is illustrated by the data in Tables IV and V. The final
potentials listed in Table IV illustrate the true potential range attained by active mild steel in white liquor. At any one temperature this range is extremely narrow; only a few millivolts. The corrosion rates are relatively low; once the depolarizers (polysulfides and possibly thiosulfate) originally present are used up (reduced), the corrosion current slows down and ceases to flow, the corrosion diminishes, and the electrode becomes more highly polarized. The experiments represented by Table V show that the steel electrode does not become so highly polarized in the presence of oxygen and that the corrosion is greater than when oxygen is excluded. This is interpreted as caused by the continuous supply of depolarizers furnished by oxidation of sulfide by oxygen. The obvious conclusion is that atmospheric oxygen acts indirectly as a cathodic depolarizer when steel corrodes in kraft white liquor. This is true at least in the initial stages of a kraft cook until all the oxygen in the digester is absorbed by the liquor.

POLARIZATION EXPERIMENTS

Figure 21 is representative of several polarization experiments. Only cathodic polarization curves were made; that is, the steel electrodes was used as a cathode in the electrolysis cell. Two curves are shown in Figure 21; the upper curve was made while periodically increasing the e.m.f. applied to the electrolysis cell; the lower curve was made by decreasing the applied e.m.f. after the maximum in the upper curve had been reached. If the above procedure were applied to a completely reversible cell, only one curve would be obtained; the curve obtained by decreasing the applied voltage would retrace the one made by increasing the applied voltage. This demonstrates the irreversibility of the electrolytic corrosion of digester steel in kraft white liquor. The flat portion of both curves is due to the evolution of hydrogen from the liquor, and the difference in voltage between the two
curves is explained as follows: When the steel electrode is placed in white liquor, a film of iron sulfide begins to form, but its formation is increasingly hindered by the increased reducing action of the increased applied cathodic potential, and the hydrogen overpotential, represented by the flat portion of the curve, is the result of a mixture of the hydrogen overpotentials on the steel electrode and on the iron sulfide. When the applied e.m.f. is decreased, the iron sulfide is given more of a chance to cover the steel electrode. Hence the flat portion of this curve is increasingly affected by the hydrogen overpotential on iron sulfide. It is apparent that the hydrogen overpotential on steel in white liquor is greater than on iron sulfide.

Figure 22, as explained in the Experimental section of this report, is a complete polarization curve obtained by combining the lower curve in Figure 22 with one of Mueller's (19) anodic curves obtained also by decreasing the applied e.m.f. At current density zero, it can be seen that the two curves meet, forming a continuous and complete polarization curve of steel in white liquor. It is presented here as an example of the type of polarization curve to be obtained in future work when adequate instrumentation is available.
CONCLUSIONS

At this time, few conclusions can be arrived at that can be completely substantiated by experimental data. A few simple tentative conclusions, based on the literature and the experimental results, can be stated, however.

KRAFT WHITE LIQUOR

The effect on digester corrosion of sodium hydroxide, sodium sulfide, sodium sulfite, sodium thiosulfate, and polysulfides has been fairly well stated by Haegland and Roald (9), Mueller (7, 10), and Roald (40). Polysulfides and thiosulfate have been found to stimulate corrosion by acting as cathodic depolarizers. Sodium hydroxide, sodium sulfide, sodium sulfite, and sodium thiosulfate seem to affect the corrosive properties of the liquor mainly by affecting the equilibrium of Reaction (3) which determines the polysulfide concentration in the liquor.

\[ S^{2-} + S_2O_3^{2-} = S_2^{2-} + SO_3^{2-} \] (3)

The sodium hydroxide concentration affects the equilibrium of the above reaction by determining the amount of unhydrolized sodium sulfide in the liquor according to Reaction (4).

\[ S^{2-} + H_2O = HS^- + OH^- \] (4)

The above views are mainly those of Haegland and Roald (9) with which Mueller (10) seems to agree, except that Mueller claims that thiosulfate is also a cathodic depolarizer in kraft white liquor. Haegland and Roald did not make that conclusion, but found that the action of thiosulfate was limited to affecting the polysulfide concentration in Reaction (3). Nor does Mueller offer experimental evidence that thiosulfate acts directly
as a cathodic depolarizer. Thus, the corrosive action of thiosulfate in kraft white liquor seems to be somewhat in doubt.

Aside from affecting the distribution of the sulfur compounds in white liquor, sodium hydroxide alone does not seem to be a corrosive agent in the kraft pulping process. A study of the work of Pourbaix (28) leads one to this conclusion.

Another indication that polysulfides abet the corrosion of digester steel, aside from their depolarizing action, is that iron sulfides are relatively soluble in aqueous polysulfides (30). If this is so, then the protective sulfide film on the digester wall would be removed to some extent by the solvent action of polysulfides in white liquor.

In the light of present knowledge, the following may be stated concerning the corrosive action on mild steel of the individual electrolytes in kraft white liquor:

**Sodium Hydroxide**

Its corrosive action is mainly limited to the effect it has on determining the concentration of unhydrolyzed sodium sulfide. It is not a primary cause of corrosion.

**Sodium Sulfide, Sulfite, and Thiosulfate**

These compounds are not corrosive to mild steel in white liquor, but affect that corrosion by determining the concentration of polysulfides according to Reaction (3). As explained above, there is some doubt as to whether or not thiosulfate acts directly as a cathodic depolarizer. From
the measurement of single electrode potentials in pure thiosulfate solutions and the accompanying observed results, it might be thought that thiosulfate is a very corrosive agent, but, as was explained earlier, the corrosive action of thiosulfate is due to its decomposition products in acid solution. In even slightly alkaline solution, however, thiosulfate does not decompose to form corrosive products (29), so the type of corrosion by thiosulfate described earlier does not occur in kraft white liquor, which is strongly alkaline.

**Sodium Polysulfides**

Polysulfides are the cause of most of the corrosion of mild steel in kraft white liquor. They act as cathodic depolarizers and stimulate the corrosion process.

**Sodium Chloride, Carbonate, and Sulfate**

These three minor constituents of kraft white liquor have received the least attention in digester corrosion studies. A study of the abstracts in the Appendix leads one to the conclusion that carbonate and sulfate are quite often used as inhibitors of corrosion and therefore cannot increase the corrosive properties of kraft white liquor. Sodium chloride, however, is generally considered a rather corrosive salt in aqueous solution. Again, a study of the Appendix shows that the corrosive action of chlorides is greatly inhibited by the presence of alkalies, especially sodium hydroxide; this is the case in kraft white liquor. The results of weight-loss tests presented earlier also indicated that corrosion of mild steel, even in slightly acid solutions of pure sulfate and chloride, in the dilute concentrations obtaining in white liquor is very low. No investigations were made
concerning sodium carbonate, but it may be predicted that its corrosive power in white liquor is very slight.

NEUTRAL SULFITE COOKING LIQUOR

Much of what is known about the corrosive properties of the constituents of kraft white liquor can be applied to neutral sulfite cooking liquor, but it is necessary to substantiate predictions by experimental results.

Sodium Sulfite

This is the primary constituent of neutral sulfite cooking liquor, and from the measurement of single electrode potentials in pure solutions of this salt, it may be stated that corrosion rates of mild steel in it would be very low. Future weight-loss determinations will tell a more accurate story.

Sodium Carbonate

Sodium carbonate is the secondary constituent of neutral sulfite cooking liquor, and by hydrolysis, some of the carbonate usually exists as bicarbonate. Again, a prediction may be made on the basis of the literature that its corrosive action would be very low in neutral sulfite cooking liquor.

Sodium Sulfate and Chloride

The same might be said in a tentative way about the corrosive action of these salts in neutral sulfite cooking liquor as was said regarding them in kraft white liquor.
Sodium Thiosulfate

A preliminary exploration of the corrosive properties of thiosulfate in neutral sulfite cooking liquor was made by the method of single electrode potential measurements. The indications are that it promotes passivation of the metal by assisting in the build-up of a protective film, but it will not be known if this is true until suitable polarization experiments are made.

Sodium Hydrosulfide

This salt may be present in neutral sulfite cooking liquor if (a) smelt from the recovery furnace is used as buffer chemical, (b) independent neutral sulfite recovery is practiced and conversion to sulfite of sodium sulfide in the recovered liquor is incomplete. No experiments were made in regard to its presence in neutral sulfite cooking liquor, but by analogy with kraft white liquor, one would expect it to form a protective film of iron sulfide on the digester wall.

GENERAL CONCLUSIONS

Oxygen affects the potential of active steel in white liquor by acting indirectly as a cathodic depolarizer. This is in agreement with Mueller's (10) theory, although he offered no experimental evidence and apparently believed that the effect of the presence of oxygen was not as pronounced as the experimental results show it to be.

The study of and use of the weight-loss test by total immersion is in a state of flux and no conclusion can be made as yet concerning a reliable and reproducible method.
FUTURE WORK

It is intended that the investigation of corrosion should continue along much the same line as outlined in this report, i.e., using the methods of weight-loss testing and single electrode potential measurements. Also, a series of polarization experiments will be initiated that are intended to illuminate some of the results obtained thus far.

One of the problems associated with using the polarization-curve technique in corrosion research is that of proper interpretation of the curves obtained. As pointed out by Mueller (10), it is not always necessary to actually record both cathodic and anodic portions of the complete curve if one is able to properly interpret one portion. Mueller chooses to record only the anodic curves and calculate the effect of variables on the cathodic portion, using a combination of known facts and assumptions in his calculations. While this is not inadmissible, the making of assumptions always has its limitations.

One of the major assumptions made by Mueller in his calculation of corrosion and depolarization curves was that iron dissolves to the ferric state, leaving behind in the metal electrode three valence electrons for every iron atom dissolved. Although this assumption is contrary to the most common assumption that iron dissolves to the ferrous state in white liquor, he apparently substantiates his assumption by calculating the corrosion current under conditions of low depolarization current and obtains a number close to 2.5 for the number of electrons released per atom of iron dissolved.

One must agree that Mueller's assumption is therefore a reasonable one and perhaps close to the truth, but it can also be readily seen that
quantitative interpretation of polarization data is not possible unless it is known exactly how many electrons per atom iron releases when it dissolves in corrosion processes.

A passage in Evans' monograph (42) on corrosion outlines some of the conditions under which iron can dissolve to either the ferrous or the ferric state: "Where metal can form more than one series of compounds, a high current density involves an abnormal drainage of electrons, producing ions of higher positive charge than those produced at low current density. If a low E.M.F. is applied to a cell consisting of two vertical plates of iron in a potassium chloride solution, the anode dissolves smoothly, forming colorless ferrous chloride. If almost the whole of the anode surface is covered with wax and the metal is exposed along a narrow line scratched through the wax, the local anodic current density becomes very high, and three electrons instead of two are abstracted for every iron atom. Consequently, a wisp of yellow ferric chloride solution is seen to descend from the scratch line....In alkaline solution, cobalt and manganese (also iron, at high temperatures and high concentrations of alkali) dissolve anodically in the divalent condition at low current densities, but at elevated current densities, higher oxides ($\text{Fe}_3\text{O}_4$, $\text{Co}_3\text{O}_4$, $\text{MnO}_2$), or even soluble compounds such as ferrates or manganates, appear."

It can be seen, therefore, that the dissolution of iron by corrosion in kraft white liquor (also the anodic dissolution of iron in polarization experiments in kraft white liquor) quite probably consists of the iron going to the divalent state at low temperatures and low current densities and, as the conditions change, to the trivalent state at higher temperatures and higher current densities. The conditions change sufficiently in a kraft
cook and also in the experimental determination of polarization curves to meet the apparent requirements for iron to dissolve in both valence states.

In view of the primary importance of an accurate knowledge of the valence state in which iron dissolves for quantitative interpretation of corrosion mechanisms as revealed by polarization experiments, it is proposed that a serious effort be made in the immediate future to determine the exact conditions under which iron, in kraft white liquor and in neutral sulfite cooking liquor, dissolves to the ferrous or the ferric state. The main conditions that apparently affect the valence state are alkalinity and temperature of the liquor, and the anodic current density.

As mentioned earlier, Lingane (17) used a method of voltammetry at constant voltage to determine the number of electrons involved in an electrode reaction by means of the following equation:

\[
W = \frac{m \cdot Q}{nF},
\]

where
\(W\) = weight of electrolyzed substance;
\(W_m\) = atomic or molecular weight of electrolyzed substance;
\(Q\) = quantity of electricity used in electrolysis
\(n\) = number of electrons per mole or atom involved in the anode reaction; and
\(F\) = the faraday (96,484 coulombs),
which is a simple statement of Faraday's law of electrolysis.

The above equation may be used to determine \(n\) if all the other quantities are known. \(W\) and \(W_m\) may be defined very accurately by the use of a pure iron anode and by an accurate measurement of the weight of the anode before and after electrolysis. \(Q\) may also be measured very accurately
by means of a suitable coulometer under conditions of one hundred per cent current efficiency, and $F$ is an accurately known constant. Thus, $n$ is the sole unknown and may be determined by solving the equation.

The foregoing is a simplified presentation of the need for accurate knowledge of the number of valence electrons released by the dissolution of an iron atom when mild steel is corroded in kraft white liquor and neutral sulfite cooking liquor, and the proposed method for determining this in the laboratory. Several experimental difficulties are expected to be encountered such as achieving one hundred per cent current efficiency, removal of iron sulfide deposits on the anode after electrolysis, prevention of the onset of passivity of the anode, etc. However, it is believed that these difficulties may be overcome and the desired results obtained.

It is further believed that the results of the proposed work would constitute a significant and lasting contribution to the further understanding of the mechanism of alkaline digester corrosion, and that, until such knowledge is gained concerning the valence state of anodically dissolved iron, quantitative interpretation of corrosion mechanisms in alkaline digesters, especially with reference to the mechanism of the action of cathodic depolarizers, can only be mostly speculative.
34. Tödt, F., Elektrochem. 41:270-3(1936).
APPENDIX

The following bibliography is arranged in the general subject order of NaOH, Na₂S, Na₂SO₃, Na₂S₂O₃, Na₂SO₄, Na₂CO₃, and NaHCO₃, NaCl, and miscellaneous. It is obvious that there will be much overlapping, but this is necessary to avoid duplication.


U-shaped specimens, made from strip and loaded by tightening a bolt and nut to decrease the distance between the prongs by a measured amount, were used in the test. Effect of compn. and heat-treatment were studied, as well as the effect of cold-work and mech. surface treatment. The customary way of employing such specimens is essentially a const.-strain test, as in the Krupp method, an appropriate test for materials used in constructions where initial stresses are largely relieved by creep in operation. Three other methods aiming at const.-stress conditions were studied. Two of these, involving a controlled stepwise increase in applied stress with time of exposure, appear particularly suited for rapid detn. of a materials resistance to the combined action of stress and corrosive attack.


Inhibition of corrosion of Fe by anodic polarization in 0.1N NaOH in the presence and absence of air is shown to result from the formation of a cubic oxide having the compn. of Fe₃C, γ-Fe₂O₃, or an intermediate comp. The cubic oxide is indistinguishable from the air-formed film. Weak areas in the air-formed film are repaired by production of this oxide. Freshly abraded mild steel becomes passive when immersed in 0.1N NaOH contg. O because of the formation of a film of Fe(OH)₂ which then reacts with O to form the cubic oxide.


To 20% NaOH soln. (partly spent from washing gasoline in the refinery) is added 1% Na₂S₂O₃·5H₂O, which prevents the formation of ppts. and colored cmpds. and inhibits corrosion of equipment when the soln. is regenerated by boiling. Other alkali thiosulfates may be used.


Various theories of intercryst. corrosion due to caustic solns. are reviewed. The most acceptable explanation appears to be one based on the distorted nature of ferrite in the region of grain boundaries,
as has been suggested for intercryst. cracking in nitrate solns. Since it has been shown that strain moves the polarization curve of Fe in the anodic direction, it follows that selective attack along the grain boundaries is to be expected; there is no reason to expect that the shift of the polarization curve by strain is peculiar to one type of anodic reaction. Carbide particles may not be required to achieve this in the presence of caustic solns., although, presumably, intergranular cementite would have a deleterious effect. More data are required to prove or disprove this theory: A study should be made of the reproducibility and disadvantages of methods of test in which the specimen contains or is immersed in large vols. of concd. caustic soln. The effect of temp. should be studied as well as the influence of the compn. and heat-treatment of the steel, and a more complete exam. made of the types of cracking produced in actual boiler failures. Chem. and phys. means of preventing the action of NaOH on boiler steels are discussed. Boiler failures still occur in spite of the inhibitive treatment of water. The elimination of riveted seams by welding is not considered desirable for locomotive boilers. Failures in riveted boilers is frequently associated with regions where alignment of the riveting holes has been bad, the riveting pressure excessive, or the caulking heavy; the elimination of such practices would be helpful. In several instances the hammer peening of patches has been helpful in prolonging the life of the steel.


The results are presented of an industrial survey on the failure of materials in alk. solns., largely dealing with NaOH. The relationship of temp. and concn. to failure can be expressed only in an approx. manner. To prevent stress corrosion cracking, the following recommendations were made, based on actual plant practice: decrease residual and applied stress, decrease temp., change materials of construction, and apply protective coatings. Points requiring further attention are outlined.


The corrosion of Fe metals in a solution of boiling 5-50% caustic alkali is prevented by adding from 0.01 to 5% (preferably about 1%) NaNO₃. This inhibitor is especially useful in preventing corrosion during the regeneration of strong alkali sweetening solns. for hydro-carbon oils. These solns. contain lg. amts. of alkali, soly. promoters, and oxidation catalysts, as well as impurities from the oils.

When Fe, freed from its original air-formed oxide film, is immersed in 0.1 N NaOH contg. dissolved O, it becomes covered as shown by electron diffraction with a thin film of $\gamma$-Fe$_2$O$_3$. The view is put forward that this film is responsible for passivity and results from a heterogeneous reaction between O dissolved in the soln. and Fe. A de-aerated soln. of 0.1 N NaOH attacks Fe very slowly. The reaction is controlled mainly by high polarization of the cathodic discharge of $H^+$ ions. The potential of an Fe specimen in 0.1 N $K_2$CrO$_4$ is unaffected by dissolved O. It appears that $K_2$CrO$_4$ can oxidize the surface of film-free Fe to $\gamma$-Fe$_2$O$_3$ in the absence of dissolved O by the heterogeneous mechanism previously suggested.


Stress-corrosion tests were carried out in app. specially designed for these tests at high temp., and similar to that of Schroeder and Berk. The specimens, of hollow form, were inserted into the base of an autoclave and loaded by means of a lever system, through a push rod inserted in the specimen. This arrangement permitted the production of accurate notch-forms on the external surface in contact with the NaOH soln. Failures, comparable with those in practice, may be produced under controlled lab. conditions with considerable consistency, but are confined to non-homogeneously stressed specimens. Concd. NaOH solns. are more effective than dil. solns. though failure has been obtained with less than 10% NaOH. Analytically pure NaOH solns. are as effective as solns. prepd. from com. product; Si is not necessary to produce failure, nor does it stimulate it. The presence of tannin does not entirely prevent cracking, though it does to some extent in practice. Anodic polarization does not prevent and may even stimulate intercrys. failure. Cathodic polarization is effective; in the only case where spontaneous failure occurred it was not accompanied by intercrys. cracks. A fine-grained steel of low C content was no more resistant to attack than a normal steel of the same C content, but a fine-grained steel slightly enriched in C showed a remarkably improved resistance.


Under certain conditions cathodic treatment facilitates rather than prevents corrosion. Activity of Fe in alk. soln. was demonstrated by means of specific org. and inorg. agents. 19 refs.


Corrosion studies on Fe (usually in the form of 0.2 mm. diam. piano wire) were made in solns. of NaOH at temps. between about 30 and 110° in
an effort to det. the effect of temp., NaOH concn., and Fe potential on the corrosion rate. These data have been obtained both for electrically insulated Fe and Fe used as an anode. Thermodynamic considerations permit a rapid prediction of the circumstances under which the Fe will be corroded from the p.d. between the Fe and a reversible H electrode in an O-free soln. The exptl. technique used is applicable to all O-free solns. to detn. the effect of temp. and concn. The corrosion of Fe in pure NaOH solns. occurs only over a definite potential range, varying somewhat with temp. and NaOH concn. Curves are presented for temps. of 80, 95, and 105° and concns. of NaOH from 0 to 700 g. per l.; extreme potential values for the corrosive range fall between -0.7 and -1.0 v. At potentials within the corrosive range the corrosion progresses continuously and gives rise to a green soln. of sodium hypoferrite (Na₂FeO₄); the latter can decomp. with the formation of a black oxide (Fe₃O₄?). The corrosion of soft annealed steel in NaOH solns. is not intercryst. At low temps. and low NaOH concns., oxidizing agents act as passifiers; at high temps. and high NaOH concns. they act as activators; in the latter case differential oxidation by air or other oxidizing agents will cause intense activation. Certain Fe alloys with a high percentage of another metal (such as the Cr-Ni steel alloy V2A) have a very nearly perfect resistance to hot concd. NaOH solns.


Corrosion data are given on welded seams of soft steel during the evapn. of alkalies in the presence of NaCl. A clearly defined passivation of the metal was observed. Most-resistant welds were obtained with seams made by soft-steel electrodes without any addn. of Ni. Parts of the samples in contact with the air were covered uniformly with an oxide film. The immersed parts were covered with rust spots. The passivation of the metal took place in the presence of an excess of Cl⁻. The presence of NaCl and an insufficient amt. of OH⁻ in the soln. with a non-uniform aeration led to the formation of FeCl₂ and Fe(OH)₂, which later was oxidized to Fe(OH)₃. ClO₃ ion facilitated the passivation. The results of the investigation were used as the basis for the construction of welded evaporators.

The chem. and electrochem. behavior of iron toward H₂O and alk. solns. is given. The corrosion of Fe in strong alk. solns. was investigated. The solution of Fe in strong hot soln. is detd. by the base potential of Fe and the formation of complex Fe⁺⁺⁺ hydroxo anions. Definite hydroxoferroates could be isolated from ferroate solns. Oxidation of ferroate solns. under various conditions gave well-crystd., colorless hydroxoferrites and 2 isomeric metaferrites having the formula NaFeO₂ which differed in color and chem. behavior. In the solns. of strong alkalies the tri-valent Fe is present as hydroxo anion. The green or red coloration of Fe contg. alkali caused by the addition of Na₂S is due to the formation of thichydroxo-ferroate or ferrite. The perferrates described by Goralevich could not be prepared according to his directions. Exptl. data and 23 references are given.


The results of corrosion tests on various metals with aq. and fused NaOH + Na₂O₂ (5%) are given. For concd. and fused NaOH the use of cast Fe contg. C 2.6-3.0, Si 0.8-1.4, Ni 18.0-22.0, and Cr 2.0-4.0% is indicated, but the use of 5 in the final processing of fused NaOH tends to offset the advantage of high Ni content of caustic-pot Fe.


Various steels were studied as powders in liquid water at 310°C. Below 1% NaCl, alloy steels showed no advantage over soft C steel, above that, Cr-Ni steel especially showed about half the corrosion. MgSO₄ reduces corrosion slightly. All but Cr-Ni steels were embrittled by strong solns.


A discussion of high-Si steels with some data on corrosion by acids and alkalies.


An account of expts. is given, and the mechanism of the resistance is considered.

18. Fershke, K. V., and Popova, L. Investigation on corrosion and factors governing the selection of alloys in the construction of equipment for the
manufacture of caustic soda and caustic potash. *Chimie and Industrie* Spec-
ial No. 232-6 (Mar., 1930).

After a brief review of the literature on corrosion of iron by alkalies, results of corrosion expts. by NaOH and KOH (950 g. per l. and 12 g. Na₂CO₃ and NaCl) for 6 hrs. at 160-400° are given, showing that, with gray cast Fe, the main factor in resistance to corrosion is homogeneity of structure, and compn. is of secondary importance. Addn. of Ni reduces the corrosion, which is completely stopped with 12½ or more of Ni. Addn. of Cr is less effective, particularly against the action of KOH. Addn. of 6% Ni and 5% Cr is equiv. to 12½ Ni. On the whole, corrosion by KOH is 2.5-3 times as great as that by NaOH. Cu is satisfactory for the piping and fittings, as far as resistance to corrosion is concerned, but is too soft; the most satisfactory alloy was found to be obtained by addn. of 21½ Ni to Cu.

---


The applicability of c.d. measurements to the detn. of dissolved O content and of the rust-preventing power of solns. is tested. The c.d. values make possible the prediction of the corroding or rust-
preventing power of the soln. Practical applications are discussed.

---


A critical resume of the work of Perl. Staudinger and Flagge [Ver. deut. Ing. Forschungsarbeiten 295 (1927)] on the action of solns. on Fe at high temp. and pressures.

---

21. Speller, F. N., and Texter, C. R. Effect of alkaline solutions on the cor-

By using the amt. of O consumed as a measure of corrosion, the effect of alky. was as follows: (1) the initial corrosion rate was the same independent of alky.; (2) the corrosion rate decreased with time, probably due to formation of a protective film; (3) the rate of film formation and degree of protectiveness increased with increasing alky.; (4) both tap and disd. H₂O gave the same results.

---


A voluminous, hard, black corrosion product in an iron pipe carrying septic-tank effluent gave, on analysis, iron oxide, ferrous sulfide, and iron disulfide, as the main components. The iron was graphitized to an av. depth of 0.25 inch. Other sulfide-contg. en-
vironments, severe on piping, are collecting systems, sludge digestion tanks, bottom compartments of Imhoff tanks, oil-field wastes, soils containing (coal tar) corrosion), and
gaseous atms. contg. H₂S above sewage. Lab expts. showed that Fe immersed in sulfide solns. under anaerobic conditions, or in digesting sludge, corroded at rates too slow for importance. Hence serious attack depends on presence of oxygen or a metallic circuit for galvanic corrosion. Protection is afforded by bituminous wrappings, cellulose-ester sheeting, cement lining, acid-proof cements in partly-filled pipes, elimination of sulfides from sewage, designing exposed iron structure for replaceability, and cathodic protection.


Quant. data are given on corrosion rates for Al, cast iron and carbon steel, ceramics, fused silica, Cr, Cu, Cu alloys, Pb, Mg, Mn, Ni, Ni alloys, Pt, Ag, Ag alloys, and stainless steel in liquid sulfur.


Qual. values are given for the following chemicals: AcOH, Ac₂O, alum, AlCl₃, Al₂(SO₄)₃, amines, NH₃, NH₄OH, NH₄Cl, ammonium phosphate, (NH₄)₂SO₄, C₆H₆, Fe₃BO₃, Br, CsCl₂, Ca(C1O)₂, CCl₄, H₂SO₃, ClCH₂CO₂H, CI, chloride, citric acid, CuSO₄, fatty acids, FeCl₃, Fe₂(SO₄)₃, Fe₃O₄, C₂H₄O₂, hydrocarbons (aliphatic), hydrocarbons (aromatic), HCl, H₂O₂, HF, I, lactic acid, MgCl₂, mixed acid (less than 20% H₂O and more than 15% H₂SO₄), MnO₃, oleic acid, (CO₂H)₂, PhOH, cresol and similar acids, phthalic acid, phthalic anhydride, Na₂CO₃, NaHSO₃, Na₄carbonate, NaCl, NaOH, NaClO, NaNO₃, Na₂SO₄, Na₂SO₃, Na₂S₂O₃, Na₂S₂O₅, stearic acid, S, SO₃, H₂SO₄, H₂SO₃, trichlorethylene.


Corrosion prevention in the production of petroleum products is effected by the addition of P₂S₂, HMS, H₂SO₃, where P stands for alkyl, aryl, or benzyl, and M is a univalent alkali metal.


The rate of soly. of Fe limited by Na₂SO₃ is found to be a function of the pH value; c. ds. measured between Fe and Pt, and Cs and Pt, show the same behavior, so that in the soln. of Fe, as well as with the cathodically polarized Pt electrode, a reduction of the sulfite by sepd. H ions is assumed. The poisoning action of Na₂SO₃ on the Pt electrode shows the same dependence on pH value. A high C content causes in the Fe a decided dependence of rate of soly. on the pH value even in reactions where pure Fe is practically independent of pH.

The theory of formation of $S_2S_4O_8$ and persulfates is considered from several points of view. Anode reactions are given for solns. of $Na_2SO_4$, $Fe_2SO_4$, $Na_2SO_3$, and $Na_2S_2O_3$. The formation of persulfate and of tetrathionate ions is shown as the polymerization of partially discharged ions. Conclusion: There is no justification for assuming that, in the formation of $S_2S_4O_8$, the mechanism is $2SCu + O + H_2O \rightarrow S_2S_4O_8 + 2OH^-$. 


A method is presented for circulating $H_2O$-$Na_2SO_3$ through a boiler during stand-by periods. It was found that a concn. of 7 grains per gallon was sufficient to maintain water and steam surfaces free of $O_2$ pitting and other corrosion. Two lb. per week of make-up $Na_2SO_3$ was needed in the boiler studied, 15,000 gallons of water being required to fill the boiler tubes, satd. steam line, economizer, water walls, headers, and all accessory piping. A weekly circulation period of 12 hrs. was sufficient to provide a uniform conc.


Petrov found that corrosion of hydraulic equipment by $O_2$ in water could be effectively counteracted by adding to the water $Na_2SO_3$ in 85-100 mg./l. excess over the eq. amt. of $O_2$ dissolved.


Inhibitors studied in conjunction with $NaNO_2$ include $KH_2PO_4$, $Na_2HPO_4$, Na hexametaphosphate, $Na_2CO_3$, $NaHCO_3$, Zn acetate, $ZnSO_4$, $Zn(NO_3)_2$, $Na_2SO_3$, and $Na_2S_2O_3$. Addn. of small amts. of $KH_2PO_4$ and $Na_2HPO_4$ to 5% $NaNO_3$ prevented corrosion of steel when it was the only metal present, without the deposition of any large amt. of inhibitor. The phosphates act as anodic inhibitors but also act as cathodic stimulators, probably because of their ability to act as buffer solns. Na hexametaphosphate gives a high degree of protection when 0.05% is added to 5% $NaNO_3$. Addn. of 0.01% $Na_2CO_3$ to the mixt. further increased the efficiency. Na hexametaphosphate is an anodic inhibitor and gives slight cathodic stimulation, which is completely suppressed by a trace of $CO_3^{2-}$. Addn. of 0.05% $NaNO_2$ gave efficient protection. Addn. of an appreciable amt. of Zn salts to $NO_2^-$ gave complete protection, but the cathodic action of the Zn was small in relation to the anodic of the $NO_2^-$. $Na_2SO_3$, which is a strong cathodic inhibitor, increases the efficiency of $NO_2^-$, but owing to the decay of the $SO_3^{2-}$ the effect is not permanent.

Its use as an O scavenger is reviewed.


An electron-diffraction study of the effect of inhibitors on corrosion of carbon steel.

The corrosion of steel, contg. C 0.12, Mn 0.35, Si 0.07, P 0.06, S 0.04, and Cu 0.02%, with disol. H_2O and with 5% NaCl soln. was examined by electron diffraction. Inhibitors used were K_2Cr_2O_7, NaNO_2, Na_2SO_3, Na_2HPO_4, and ZnSO_4 in 0.01% to 1% solns. A chart shows the corrosion products for each case. NaHPO_4 and ZnSO_4 were most influential. In general, the surface product is Y-Fe_2O_3·H_2O with underlying Y-Fe_2O_3. Hydroxide was not detected except in the case of Na_2HPO_4 which gave a yellowish white ppt. of colloidal Fe(OH)_3. The process in these solns. is considered as follows:

Fe(OH)_2 [or Fe(OH)_3] → Y-Fe_2O_3·H_2O ↔ T.P.S. → Y-Fe_2O_3

2FeO·Fe_2O_3·H_2O

T.P.S. is an intermediate product from Y-Fe_2O_3·H_2O to Y-Fe_2O_3.
Depending on which way the equil. is shifted, the passive (to the right) and active (to the left) states of steel appear.


Expts. were performed with solns. of Al_2(SCN)_2, (NH_4)_2SO_4, BaCl_2, MgCl_2, FeSCN, FeSO_4, KCl, KNO_3, K_2SO_4, NaCl, NaNO_3, and Na_2SO_4. As a general rule, the corrosive power of the concd. solns. was found to be less than that of pure water. As the temp. rises, the rate of corrosion increases rapidly but, with the exception of (NH_4)_2SO_4 solns., the corrosive power does not increase as rapidly as does that of pure water. Probably for every concn. there is some temp. (which in some cases is below 0°C) at which the corrosive power of the soln. is equal to that of pure water. Below this temp. the soln. will have greater corrosive power than that of water and above it less. The more dil. the soln., the higher the temp. at which the corrosive power is equal to that of water, and for this reason very small amts. of impurity may cause increased corrosion of boilers.


A systematic detn. of iron, bronze, and brass corrosion in resting
and moving solns. of MgCl₂, NaCl, MgSO₄, Na₂SO₄, CaCl₂, various mixts. of these, in potash waste liquors, in various river waters and in distd. water. A number of tables are given including the exact data for salt concns. used, analysis of the potash waste liquor and the corrosion results obtained over a period of 30 days. The following conclusions are drawn: Bronze and brass are only lightly attacked by the salts and waters. Mg salts at ord. temp. in a concn. corresponding to 112-9 German degrees of hardness are not dangerous to iron. Mg salts in the feed water to the steam boiler must be regarded as a danger, increasingly so with the concn. The explanation of this is given in the hydrolytic decomn. of Mg salts at high temp. and press., producing the effects of acid.

35. Berl, E., and von Taack, F. The protective action of sodium sulfate on the attack of ingot iron by alkalies and salts under high pressure. Arch. Wärme-
wirt. 9, 165-9(1928).

Tests 7.5 hrs. long were made on powd. ingot Fe in a bomb at 260-
360°C. After the test, alkyl. of the soln., loss of Fe and gain in O of the powder, and H₂ were detd. Up to about 0.02 N concn., NaOH decreases the corrosion of pure water; above this the corrosion rises rapidly.

When Na₂SO₄ is added in any amount from 0.01 to 0.9 mol. per l., the corrosion for any concn. of NaOH remains below that for pure H₂O. NaCl is weakly corrosive and does not affect the action of NaOH. NaNO₃ evolves NO instead of H₂, and is moderately corrosive but inhibits NaOH to some extent; Na₂HPO₄ is more corrosive and a better inhibitor. Na₂S is very corrosive. Roentgen spectra show that the only oxides formed are FeO and Fe₂O₃. The effect of sulfate is perhaps due to the formation of a firm oxide film.


The expts. show that the results are influenced by the oxide layer which occurs naturally on Fe. The formation of this film is exceedingly fast in the air as well as in electrolytes satd. with air. The time of passivity was detd. on Fe free from this oxide film and the same relation as with H₂SO₄ was found.

37. Berl, E., and von Taack, F. Causes of the protection afforded by sulfates against the attack of boiler plate by salt solutions. Arch. Wärme-
wirt. 10, 337-9(1929).

Tests were made in a high-pressure bomb. Only a summary of results is given. Pure water attacks ingot iron slightly. NaCl up to 0.02 N decreases corrosion; beyond this, corrosion again increases greatly. Na₂SO₄ inhibits this increase. The action is not due to reduction of the sulfate; no reduction products were found. Na₂HPO₄ affords some protection; MgSO₄ has little action. MgCl₂ causes much corrosion by decomp. to give free acid; Na₂SC₄ has some inhibiting
action in this case also. Nitrites and chromates have a similar effect. The action of NaOH is probably catalytic, and due to the intermediate formation of ferrites. Na₂SO₄ acts by causing ptn. of a protecting oxide film on the iron. NaCl delays this ptn. and therefore increases corrosion. In the case of MgCl₂ the Na₂SO₄ acts by reducing the pH value of HCl soln.; this effect was verified experimentally.


An investigation was made of the attack of mother liquors of sylvinite, carnallite and Glauber salts upon sheets of iron, electrolytic Cu, brass, Al, and an Al alloy contg. 3% Mn, 2.5% Mg and 0.5% Sb. The extent of corrosion was detd. by the loss of wt. method. The attack is severest with Cu and less severe with Fe. Al stood up relatively well at room temp., but is severely attacked at 95-100°C. The Al alloy showed the pit type of corrosion. With ordinary immersion methods the mother liquor of sylvinitie shows the greatest corrosiveness, the mother liquor of carnallite shows less, and the mother liquor of Glauber salt least. At high temp. the carnallite liquor is more corrosive than sylvinitie liquor, because of the disso. of the MgCl₂. By moving the sheets or the soln., the formation of protective layers in the Glauber salt soln. is disturbed. The losses of wt., therefore, are greater here than in sylvinitie liquors under similar conditions. The corrosion is diminished by the exclusion of air, and increased 2.5 times by the introduction of 0, 5.4 times by stirring the soln., and 8.6 times by heating the soln. to 95-100°C.


The app. used in previous studies has been improved by the addn. of an oscillograph for measuring time intervals. The passivation curves for Fe electrodes covered with a layer of Fe oxide (either natural or artificial) in a soln. of Na₂SO₄ have been detd. By applying Müller's theory to these data it is possible for the first time to det. separately the resistance of the pores and of the oxide film itself. As the film becomes thicker the pores become smaller and their resistance rises; the resistance of the film also increases. The free pore surface is calc. by three independent methods.


A number of solns. of various salts at varying temperatures were used in the study of their attack on various metals and alloys, and the results tabulated. Among the solns. used in the tests was one contg. 1.1 g. NaH₂SO₄, 3.5 g. Na₂CO₃, and 2 g. NaOH in one l. of H₂O tested at 100°C. Steels and cast iron were not affected by this soln. at 100°C.

Armo Fe and several non-rusting steels were investigated by electrochem. methods for their resistance to corrosion in neutral solns. of LiCl, NaCl, KCl, KBr, KI, Na$_2$SO$_4$, and K$_2$SO$_4$. For non-rusting steels definite lower threshold concns. of the attacking electrolytes were detd. The specific effects of the ions involved were recorded and likewise the effect of O$_2$ dissolved in the electrolytes.


Anodic corrosion of various kinds of steel and pure Ni in Na$_2$SO$_4$ soln. was examd. by test electrolysis with a c.d. of 12.5 amps/sq. dm. The corrosion is several hundred times greater in Na$_2$SO$_4$ than in NaOH soln. The order of durability of various metals in Na$_2$SO$_4$ is different from that in NaOH. In NaOH 18/8 Cr-Ni steel is fairly durable, while it is severely corroded in Na$_2$SO$_4$. This suggests that the anodic corrosion is quite different from the chem. corrosion in acid.


Data on Monel, Inconel, Hastelloy, Worthite, Durimet, Ni, cast iron, steel, and chemical lead in inorg. sulfate solns.


Six corroding solns. were made by dissolving NaCl, Na$_2$SO$_4$, Na chromate, trisodium phosphate, and NaC$_2$H$_3$O$_2$ in dist. H$_2$O in sep. containers, each soln. having a Na content equal to a 3% NaCl soln. Each cathode consisted of a cylindrical piece of S.H.E. 1010 steel sheet 7 in. in circumference and 2.5 in. high. The anodes were 2-1/4 in. x 1 in. x 1/16 in., cut from ingots. Each expt. lasted 24 hrs., a sample being placed in 200 ml. of soln. at 35°. The expts. showed that mild steel can be protected cathodically in solns. of certain salts at pH values between 3 and 11 and at a temp. of 35°. In all 5 solns., the Zn-Li alloy anode was equal to or superior to the Zn and Mg anodes. In all of the solns. the av. corrosion penetration per day was less with Zn than with Mg.

A study was made of the effect of $K_2Cr_2O_7$ on the cathodic polarization potentials of Fe in solns. of NaCl 25, Na$_2$SO$_4$ 57.5, Na$_2$CO$_3$ 530, NaHCO$_3$ 420, mg./l., pH 10.45, and the $K_2Cr_2O_7$ protection mechanism proposed.


Several steels have been studied for their corrosion loss in a no. of electrolytes (LiCl, NaCl, KCl, KBr, KI, Na$_2$SO$_4$, and K$_2$SO$_4$) and the results are presented in graphical form for loss in wt.


Accelerated corrosion tests were run on parkerized, bonderized and plain steel panels in solns. of Na$_2$SO$_4$, NaCl, and Na$_2$CrO$_4$. Examples are also listed of previous work done in acid, neutral, and alkali solns. and in air and gases at elevated temps. From the test results a math. formulation was developed. The reaction speed for the formation of the corrosion products is given by $k = 1/2 \ln F_A/F_O$.

The value of the rate const. $K$ is a numerically exact value for the strength and speed of attack on the metal. It was further established that the reaction rates at a local anode area are dependent upon the ratio of bare unprotected metal to the nonreactive surface area. The effect of time on the corrosion is detd. by the instability of the corrosion layer and the ease with which the cathode polarization takes place.


E.m.f. measurements are carried out with galvanic couples of common steel vs. stainless steel in N to 0.001N H$_2$SO$_4$, and 0.1N Na$_2$SO$_4$ in spontaneous corrosion is shown in schematic diagrams.


Measured over 12 hrs., the potential $E$ of Fe in a soln. of NaCl 25, Na$_2$SO$_4$ 57.5, Na$_2$CO$_3$ 164.3 mg./l., becomes increasingly negative and shows 2 arrests, one at about -120 mv. (on the $A$ scale), the other, at the end of the 12 hrs., at about -430 mv. Along the 1st portion of the curve, $E$ is detd. by the rate of cathodic reduction of O$_2$ which becomes progressively depleted around the electrode and causes strong conc. polarization. Along the 2nd branch, $E$ is detd. by the anodic process Fe $\rightarrow$ Fe$^{++}$ + 2e$^-$. In the presence of Na$_2$O$_2$, $E$ becomes in-creasingly negative with time, attaining about +250 mv. after 12 hrs.,
i.e., NaNO₃ can raise E of Fe by 700-750 mv. NaNO₃ is thus shown to be an anodic inhibitor.


The corrosion of Fe, in the presence of gum arabic, in water and in NaCl and Na₂SO₄ solns., is accompanied by the formation of a negative sol. The corrosion is accelerated by light and the presence of salts, but is usually inhibited by the gum arabic. These results are attributed to the diffusion rate of O₂, the stability of the Fe cmpds., the nature of the adsorbed films, and the peptizing and coagulating action of the media.


The severe corrosion of wrought iron condenser tubes through which hot water was flowing was found to be due to the high CO₂ content of the feed water for the boilers. The removal of the CO₂ from the feed water by a lime-soda water softener stopped the damage.


Cases of corrosion of cast iron and steel are described. Expts. with water and 0.05N solutions of NaCl, K₂CrO₄, Na₂CO₃, and NaCl + K₂CrO₄ or Na₂CO₃ show that corrosion is stopped by K₂CrO₄ and Na₂CO₃ but that when used with NaCl very serious pitting occurs.


Six inhibitors NaOH, Na₂CO₃, Na₃PO₄, K₂CrO₇, Ca(OH)₂ and Na silicate have been studied to determine the pitting effect when chlorides are present in solution. Partially immersed steel specimens were used to study the water line effect. With progressive addition of inhibitor the corrosion changed from general to localized to complete immunity. Inhibition may cause serious pitting at breaks in the scale. The quantity of inhibitor to give immunity is greater for rusted metal than for bare. Motion of the solution reduces the amount of inhibitor needed. Alkaline inhibitors should be added in amounts to neutralize acidity.


The corrosion of Fe was studied and the effects of H₂O, O₂ and CO₂ were determined. The primary cause of the corrosion of Fe is attributed to the soln. of Fe in H₂O. A film of H₂O adhering to the iron surface prevents corrosion in progress to the dissolving.
process. Oxygen acts as an accelerator; it removes Fe(OH)$_2$ and H$_2$ by oxidation. CO$_2$ also removes Fe(OH)$_2$ and accelerated the reaction by decreasing the pH.


In the absence of chlorides it was found that NaOH gave complete protection at pH above 10.3 and that the corrosion was general, with a min. about pH 3. In the presence of chlorides the pH for passivation was found as about 12.6 with general corrosion below 10.3 and local corrosion between 10.3-12.6. The presence of chromates suppressed general corrosion if the pH of the solution was such that Cr(OH)$_3$ ppts. from a solution containing chromate in the conc. present. At higher pH, local corrosion or passivation was observed, depending on the concn. of chromates and chlorides. The presence of NaHCO$_3$ or NaCO$_3$ decreases the conc. of chromate needed for protection. Recently it was observed that phosphates are more efficient than carbonates and bicarbonates in suppressing corrosion in presence of chlorides.

(See also: Pourbaix, M. [Univ. Libre. Brussels, Belge] Corrosion, passivity and passivation of iron--the roles of pH and potential. Soc. roy. Belge. et Ind., Mem., no. 1, 40 pp., 1951.)


Intense water line attack occurs on Fe partly immersed in 0.17 M NaCl containing Na$_2$HPO$_4$, Na$_2$CO$_3$, NaOH, or K$_2$CrO$_4$ inhibitor in the presence of O$_2$ without applied current and in the absence of O$_2$ with applied current.


Exposure of steel spec. to dil. soln. of common anodic inhibitors such as Na$_2$CO$_3$, Na$_2$SeO$_3$, Na$_2$HPO$_4$, and Na$_3$PO$_4$ free from and containing a low conc. of KCl could result in either generalised attack, localised attack or pitting, the latter only being obtained in carbonate containing chloride solution. It appears that the products control the form and rate of corrosion.

58. Vyskočil, A. Effect of anions on the electrolytic behavior of metals. Collection des Travaux Chimiques de Techniques 15, 1101-6(1950). (In English)

Previous expts. by V. on the corrosion of Mg and Fe are explained by the formation of local elements with absorbed anions as local anodes. Strongly adsorbed anions form a protective film, so the corrosive action is not due to the adsorptivity of the anions.
Since the anions are not consumed in the process, they may be considered to be catalysts. CO$_2$, carbonates, and salts of weak acids are as corrosive as salts of strong acids.


Dil. salt solutions absorb O faster than water. This explains the much more rapid rate of corrosion in salt soln. exposed to the air.


A series of experiments, using open hearth Fe, and common sheet iron or mild steel suspended alongside each other in distilled H$_2$O and in 10% NaCl soln. with and without air agitation, indicated no essential difference in the pieces of new Fe as contrasted with the common Fe.

Another series of experiments used 24 varieties of Fe and steel. Corrosion in H$_2$O at rest, plates not dried, produced greater losses in wt., with one exception, than in the case of 10% brine without air agitation. Corrosion increased greatly with submerged plates when the liquid was kept saturated with air.


Corrosion of Fe in tap and chlorinated mineral waters was accelerated 95 and 68% resp. at 15° owing to direct contact with FeS. In a 1% NaCl solution direct contact with FeS accelerated the corrosion by 230%. Indirect contact with a Fe wire accelerated corrosion by 470%.


Tests were undertaken to determine the influence of Mn and the corrosion of hypo-eutectoid steels. An Au cathode was used. The cathode immersed area was 40 times that of the steel specimen which was the anode. The solution was 0.2% NaCl. The progress of corrosion was observed with a microscope. Experiments were also made of the effect of oxygen. Results indicate that the purely "chemical effect" either does not exist or is extremely slow and unimportant compared with the electrochemical corrosion reaction.


Tests on the corrosion of cast iron and steel immersed in 20 g./l.
NaCl solution showed that: when the solution is not aerated both the Fe and steel lose wt. steadily and at approximately the same rate in aerated solutions. The steel loses weight somewhat more slowly than in non-aerated soln. while with cast iron the oxidation products adhere to the metal and form a protective coating.


Studying the action of the salts in sea water, G. shows that 0.3% MgCl₂ is as corrosive as 2% NaCl. Cast iron is more resistant than steel and aeration has little effect. MgSO₄ in 0.175% soln. is similar to MgCl₂ and shows no tendency to cause rusting. A 0.18% soln. CaCl₂ in aerated solns. corrodes steel, but slowly forms a protective coating on cast iron. In de-aerated solns., it rusts cast iron about twice as fast as steel.


Cast iron specimens made by two different methods and containing 0.0, 0.3, 0.41, and 0.89% Cr were used. The aqueous solutions used were those of KCl, MgCl₂, and NaCl, saturated and dilute, pure and mixed. The following conditions were varied: access of light, saturation of the solution by air, stirring of the solutions, periodic removal of rust, etc.

NaCl solns. have the maximum corroding effect. Dilute solutions are generally more corrosive than saturated, the optimum concentration being 1%. Stirring and saturation with air treble the effect. Cast iron is affected to a depth of 0.5 mm. annually under the most unfavorable conditions.


The loss of wt. of Armco Fe is tabulated for different time intervals when the Fe is exposed to water under different conditions of light and temperature, to dil. acid and various salt solutions when bubbling O through them, to different concentrations of KNO₃, Na₂CO₃, and HCl, and to solns. of the following salts: KCl, NaCl, MgCl₂, BaCl₂, KNO₃, NaNO₃, K₂SO₄, KAl(SO₄)₂, Na₂HPO₄, K₂Cr₂O₇, K₂CrO₄, KClO₃, KMnO₄.


Metals were placed in corroding solutions of various salts under conditions of total immersion in absence of air, total immersion in presence of air, partial immersion (liquid aerated),
total immersion (soln. stirred), and total immersion (temp. 95-100°C.)
corroded at the relative rates of 1, 3, 3, 5 and 3-6 respectively.
Ferrous metals were attacked most strongly while the brasses and
bronzes were attacked slightly. Corrosivity decreased as follows:
MgCl₂, carnalite, rock salt, NaCl, KCl, and FeSO₄.

68. Girard, T., Chimie & Industrie, Special no., 354-65(Febr., 1929). Action
of sea water on ferrous metals.

69. Van Müllen-Schöltten, W. The corrosion of iron in sodium chloride solutions.
Arch. Eisenhüttenw., 2, 523-30(1929).
Electrodes of (a) smooth, and (b) rough Fe were dipped into NaCl
soln., the outer circuit was completed through an ammeter. In a
quiet solution the smooth electrode becomes negative, moving the
electrodes or stirring the solution caused reversal of polarity. By
measuring single potentials involved and applying Nernst's theory of
the cell to determine the e.m.f. produced, it is shown that Fe(OH)₂
and Fe(OH)₃ formed upon the electrodes must be considered not as
separate phases, but as solid solutions. When C is admitted to the
two poles it alters the potential of both, but the relationship
Fe²⁺/Fe³⁺ does not remain alike for the two poles. Measurements
confirmed theoretical values. Similar explanations are offered for
the rusting of Fe; the previous condition of the surface, both as to
its physical state and the Fe³⁺/Fe⁺ ratio in the rust present, deter
the future course of the reaction upon it.

70. Hasegawa, K., and Hari, S. Corrosion tests of iron and steel in distilled,
tap and sea water. J. Eng. Assoc. Harbinia 7, no. 35, 27 pp.(1930); Pyo-

    Corrosion loss of 126 specimens was measured and time corrodibil-
ity curves were plotted; the longest time was 52 weeks. The corrosion
loss was the largest in distilled water and the least in tap water.


    Exsuts. were made in which mild steel disks were totally immersed
in stagnant natural sea water and 0.5 N NaCl at a const. temp. and
under 700 mm. pressure. The amounts of C absorbed and of C evolved
were measured periodically.

72. Podbursky, R. Salt effect in metal corrosion. Archiv. Chem. Forsch., 8, 97-
113(1933). (113-114 in German)

    It is concluded from experiments with Zn plates and Fe wire in
NaCl that the changes in metal potential are much more important
in the establishment of salt effect than the changes in solution
velocity for C conforming to the Adeney convection currents. Visi-
ble protective layers of corrosion products have no influence on

A dependable procedure is described by which reproducible measurements of the potential of an Fe electrode in a brine can be obtained. This procedure is employed in making a survey of the inhibiting effect on the corrosion of Fe in brine of different classes of org. compounds. Certain classes of org. compounds are shown to have a strong tendency to inhibit the corrosion of Fe in brine. The mechanism of this inhibiting action is partially elucidated.


From experiments on the rusting of Fe in H₂O and NaCl solns., T. concludes that oxidation is not due to differential aeration but is associated with surface tension effects.


Factors controlling corrosion rates of ferrous metals in stagnant solutions and a standardized system of corrosion measurements are discussed. Standardized app. and procedures are described in which the amount of O₂ absorbed and of H₂ evolved are measured periodically. Corrosion-time curves are given for NaCl and KCl solutions. Corrosion-time curves are given for NaCl and KCl solutions. Other corroding solutions were used too.


Observations made on drops of NaCl solutions of various concentrations were placed on specimens of Fe and kept in an atmosphere are described. The variations in humidity and salt concentration and the presence of dust particles explain in part the divergences of opinion between Evans, Herzog and Chaudron on the one hand and Haass and Lubreich on the other hand. The gas concn. cell theory alone cannot explain the complexities of the Evans phenomenon.

Three per cent NaCl solution was allowed to drop on samples of steel and other aluminum and magnesium alloys. The height was varied. Corrosion was greatest when the height was the greatest. The aluminum showed greater loss in tensile strength for the greatest height.


Review and summary of the author's views.


A study of the electron diffraction pattern obtained from Armco iron immersed in NaCl solutions for varying lengths of time shows that the uppermost surface is Fe$_2$O$_3$. When this is removed, there is revealed, depending on the time of immersion, an adherent layer of either FeSO$_4$ or a new substance called the "two ring" substance from its diffraction pattern. This new substance is shown probably to be intermediate in compn. between the other 2 oxides.


When Fe or Zn are partly immersed in solutions of NaCl or KCl, corrosion first occurs at a zone somewhat below the water line, and later attains a max. at the water line. A single math. equation accounts for the two different effects.


The influence of temp. upon corrosion of Fe in salt solutions was studied with the aid of the Evans cell. Rising temp. accelerates velocity of the depolarization reaction and decreases the O concn. in the cathode chamber. The corrosion velocity increases very rapidly up to a temp. of 45°C.


Specimens of mild steel were rotated at speeds up to 260 r.p.m. for varying periods in 0.5 M NaCl, "conductivity" H$_2$O, hard supply H$_2$O, and sea water. Depth of corrosion penetration and loss of wt.
of metal were subsequently determined in the specimens, and absorption and evaluation measured during the tests. The maximum rate of penetration in 0.5 NaCl was approx. 7 mm. per year at 260 r.p.m. Corrosion rate in NaCl decreased with increasing r.p.m., an explanation is offered. The mechanism is considered to be electrochemical.


Solution and potential wt. losses were measured for duplicate samples from one lot of low carbon steel. The tests were conducted in a circular path app. with aerated 3.5% NaCl as the corroding medium. The exposed area was varied by masking the edges and back of the specimens with a mixture of equal parts of white rosin and beeswax. The average solution potential was constant irrespective of exposed area. The average corrosion rate, standard deviation of corrosion rate, and standard deviation of potential measurements decreased with increasing area up to 25 sq. cm. and then remained constant for larger sample areas. Crevice corrosion at the wax-metal-liquid line is suggested as the cause of the variation of corrosion rate with area.


Discusses the galvanic coupling of a piece of Fe at high temp. to another piece at low temp. in an electrolyte. The lab. study was carried out in 3% NaCl solution.


In distilled water at speeds of 750-1500 r.p.m. (1000-2000 ft./min.) machined mild steel specimens remained virtually unattacked for 7 days, provided rotation was continuous. Stationary exposure resulted in corrosion but subsequent corrosion held the rate to a minimum. Machined mild steel in 0.1M NaCl soln. revealed, surprisingly, that passivation may occur under conditions of rapid movement, although the usual result is a very rapid widespread attack on the metal. Turned, milled or planed mild steel specimens corroded heavily in the majority of the tests; in some passivation set in for a day whence corrosion started at the edges. However corrosion was less than one third of most of the samples. Presumably there is simultaneous film breakdown and film repair. Considerable divergence between corrosion rates in different tests seems to indicate that the rust is thrown off to a different extent depending on the rotation. It is believed that the nature and adhesion of the rust is the more important factor. It is unlikely that passivity could persist for very long.

The corrosion of Fe covered by 0.5 NaCl solution and 0 atm. is examined. Owing to the combined effect of the high elec. cond. of the liquid film and the unrestricted supply of O reaching the metal surface, the results are dependent almost entirely on the corrosion properties of the metal itself. Acceleration of corrosion of the "O absorption" type may be caused by the catalytic effect of certain impurities themselves and not necessarily of oxide films on the O depolarization action. Several of the results obtained differ from those found for specimens corroding in the restricted supply of O.


Mild steel specimens, both emersed and grit blasted, were tested in 0.1 NaCl in the temp. range 22-30°C with a high speed rotor app. The corrosion rate for the emersed specimens is increased 50% in this range. Grit blasted specimens show even greater rates and temperature coefficient besides showing no passivity. The rate-controlled step seems to be chemical rather than physical.


An electrometric titration method is described in which a chloride soln. is slowly added to the soln. surrounding a ferrous metal electrode covered with a film. At a sharply defined point a change in potential takes place, an indication of the breakdown of the film. Anodic polarization increases the sensitivity toward chloride ion, whereas cathodic polarization has the opposite effect. With stainless steel electrodes greater differentiation was obtained by immersing in 11. dichromate soln. or dist. water using HCl as titrating agent. The ferrous metal specimens, which were first passivated with FeCl₃, fell into three groups, i.e., iron and steel, Cu-bearing steels, and stainless steels, each group showing a characteristic behavior under this test. A general parallelism of the amt. of chloride required to break down the film and the general experience as to the relative resistance of these three types of ferrous materials against atm. corrosion is indicated.


Potential measurements of local elements (according to Fenwick’s method) were made on steels with 0.071 to 0.41% C, 0.4 to 1% Si, 0 to 0.9% Mn, 13.5 to 20% Cr, 0 to 11.6% Ni, and 0 to 2% N, resp., which prove the usefulness of the method, can be used also for drawing conclusions with regard to the mechanism of the corrosion process.

In the process of rusting, α-FeOOH and γ-FeOOH are formed as oxidation products of iron II. The α-form results if the oxidation leads directly to Fe III. Dehydration exists on Fe rust in which the temp. is increased in steps show that, if the rust is slowly produced, its H₂O content is const. up to 160º at the amount required for FeCOOH; at higher temps. this quickly falls. Rapidly formed rust has considerably lower H₂O content even at lower temps.


The method used for crystallizing the metallic sulfide minerals consists simply of heating the components with an aq. soln. of sodium polysulfide (Na₂₇S₉), thereby dissolving the components, and then slowly cooling. The compn. of the soln., the max. temp. are adjusted until all the mineral components are dissolved during the heating part of the cycle. It has been found that the soln. increases if: the temp. increases, the d. of the soln. increases, the Na₂S concn. increases, or the free S concn. increases. It has been found that the order of solv. of the simple metallic sulfides in alkali polysulfide solns., from least to most solv., is: FeS, ZnS, Cu₂S, Ag₂S, Bi₂S₃, Au₂S, HgS, Sb₂S₃, As₂S₃. The free S content, or x in Na₂Sₓ, controls the growth of the metals, subsulfides, and polysulfides. Special bombs were used to keep the solns. at high d. and high temp.


S of average particle size 120μ was dissolved in mechanically agitated solns. of Na₂S. At regular time intervals the total S, the monosulfide, the polysulfide, the thiosulfate, and the hydrosulfide were detd. The soln. is complete in 9 hrs.; the max. value of x in Na₂Sₓ is 5. Thiosulfate, which may be present in the cryst. S added, increases as a result of oxidation. The amt. of polysulfide is linearly proportional to the total S introduced. The pH and the oxidation-reduction potentials were measured for different values of x.


From pH, measured reduction-oxidation potential, and total S, can be calculated the distribution of S in solns. of Na₂Sₓ, where x = 1-5.


Because of disagreement of results on the hydrolysis of Na₂S
obtained by methods employing conductance, pH, and $K_W/K_a$ calcns., the method of Knox was investigated; it is based on the soly. of $\text{HgS}$ in $\text{Na}_2\text{S}$ soln. and insoln. in $\text{NaOH}$, $\text{H}_2\text{S}$, and $\text{H}_2\text{O}$. $\text{HgS}$ is insoln. in $\text{NaOH}$, $\text{Na}_2\text{S}$, and $\text{H}_2\text{O}$ at 25°. At 165°, soly. in $\text{NaOH}$ is slight, and correction could be applied. In the presence of a large excess of $\text{NaOH}$ to suppress hydrolysis, soly. of $\text{HgS}$ in $\text{Na}_2\text{S}$ bears a mol. to mol. relation to concn. of $\text{Na}_2\text{S}$. Apparently $\text{HgS} + \text{Na}_2\text{S} \rightleftharpoons \text{Na}_2\text{HgS}_2$. This method applied to mixts. of $\text{Na}_2\text{S}$ and $\text{NaOH}$ gave the following results for percentage hydrolysis of $\text{Na}_2\text{S}$:

<table>
<thead>
<tr>
<th>$\text{M Na}_2\text{S}$</th>
<th>$\text{M NaOH}$</th>
<th>0.25</th>
<th>0.50</th>
<th>0.75</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>at 25°</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>92.7</td>
<td>79.7</td>
<td>66.7</td>
<td>56.8</td>
<td>37.8</td>
</tr>
<tr>
<td>0.25</td>
<td>91.9</td>
<td>80.3</td>
<td>--</td>
<td>58.7</td>
<td>41.0</td>
</tr>
<tr>
<td>0.35</td>
<td>83.8</td>
<td>71.9</td>
<td>--</td>
<td>55.1</td>
<td>33.1</td>
</tr>
<tr>
<td>at 110°</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>89.3</td>
<td>79.3</td>
<td>67.1</td>
<td>51.9</td>
<td>43.1</td>
</tr>
<tr>
<td>0.20</td>
<td>92.0</td>
<td>84.5</td>
<td>72.9</td>
<td>53.5</td>
<td>46.9</td>
</tr>
</tbody>
</table>

Application of the data to analytical data from a kraft cook indicated the following concns. at 0 time and after 165 min.; $\text{NaOH}$ 1.44, 0.34; $\text{Na}_2\text{S}$ 0.23, 0.03; $\text{Na}_2\text{CO}_3$ 0.14 and 0.23 l. equiv. conductance at infinite diln. (cm$^{-1}$ cm$^{-1}$/equiv. wt.) detd. by the methods of Koblausk and Shedlofsky, resp., are: $\text{NaOH}$ 234.6, 239.2; $\text{Na}_2\text{CO}_3$ (unhydrolyzed) 102.3, 102.8; $\text{Na}_2\text{CO}_3$, 165.7, 150.4; 1/2 $\text{Na}_2\text{CO}_3$, 132.9, 127.7; $\text{Na}_2\text{S}$ (unhydrolyzed) 104.3, 106.9; 1/2 $\text{Na}_2\text{S}$ 131.1, 133.8.


The work identifies the sharp ring substance as the green ferrosiferic corrosion product that develops at $O_2$-poor locations.


The problem of soln. of metals in electrolytes is treated mathematically. The calcns. express the theory of overpotentials; they are made on the assumption that the soln. of metals is the result of
either a direct attack on the metal by the electrolyte or a secondary reaction. On the basis of values of activation energies, coeffs. of transfer, velocities of various kinetic activities, and the structure of the electrode, it can be detd. whether the reaction is a direct soln. of a metal in an electrolyte or the result of a secondary reaction. The theoretical results were confirmed by expts. with Zn, Cd, Al, Hg, Cu, etc.


The presence of low concns. of certain reducing agents, which normally function as depolarizers, brings about very substantial increases in the potential at which O is evolved at a Pt anode. The phenomenon was studied by polarizing a clean Pt wire anode in an inert electrolyte until the potential became substantially steady; a quantity of the oxidizable substance was then added and the anode potential observed over a further period of electrolysis. The elevations of anode potentials observed after 2 min. with a variety of addn. agents, each at a concn. of 0.01M, in the electrolysis of a phosphate buffer (0.2M K$_2$HPO$_4$ + 0.2M Na$_2$HPO$_4$, pH 6.8) at 20° with an anodic c.d. of 0.15 amp./sq. cm. were: thiourea 0.63 v., NH$_2$SCN 0.59 v., Na Tetraphthionate 0.45 v., Na$_2$S 0.44 v., urea 0.41 v., Na$_3$S$_2$O$_3$ 0.37 v., thioglycolic acid 0.34 v., hydroxylamine sulfate 0.22 v., Na$_2$S$_2$O$_3$ 0.20 v., biuret 0.20 v., Na$_3$S$_2$O$_3$ 0.18 v., Na$_2$NO$_2$ 0.17 v., and metol 0.16 v. No comparable effects were observed with other oxidizable substances not contg. S or N. The effect was also observed in acid and alk. electrolytes of different types, the magnitude increasing with increasing acidity. Variations of c.d. appeared to have little effect on the magnitude of elevation, provided the working c.d. was above the limiting value for diffusion of the added substance to the anode. The effect appears to be specific for Pt; no elevation of potential was observed with Au, Pd, graphite or Hg anodes. An anode at which the potential has been raised undergoes no permanent change; rinsing with H$_2$O and inserting in fresh electrolyte gives its normal (low) potential. It appears that the effect is brought about by the added substance removing some essential intermediate in the evolution of O at a Pt anode, and so retarding the rate of electrode reaction.


Under the effect of corrosion, two kinds of layers may be formed on the surface of the iron. If the layer is impermeable to the corroding agent it is a protective one; otherwise rust is continuously formed. Besides a rust layer easily removable, a black layer of magnetite is also formed. This, however, is changed continually to limonite under further oxidizing effects; therefore, the rusting procedure must be considered as an ever continuing process. Experiments showed that if the water was acidified by CO$_2$ or made oxygen free by passing H$_2$ or N$_2$ through it, no rust formation was observed.
on the surface of iron and both the water and iron surfaces remained unchanged chemically, even though a slight continuous soln. of iron took place.