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TESTS OF CORROSION INHIBITORS FOR WATER TREATMENT IN AIR-CONDITIONING EQUIPMENT

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ABSTRACT

Treatment of the circulating water used in air-conditioning equipment with small amounts of certain chemicals and control of the pH of this water greatly reduce the losses resulting from corrosion. The order of decreasing efficiency of the inhibitors studied was (a) chromates, (b) silicates, (c) phosphates, and (d) carbonates. The differences in the corrosion resistance of the various kinds of iron and steel used were slight in comparison with the effect of a change of inhibitor or condition of test.

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I. INTRODUCTION

With the increasing use of air conditioning during recent years, the protection of the equipment against corrosion is becoming increasingly important. If suitable precautions are not taken to guard against the losses from corrosion, parts of the system become badly corroded and require replacement in a very short time. This is especially true in industrial regions, where the normal contamination of the air with acid-forming gases, as oxides of sulfur and carbon, is relatively high. The presence of chlorides in the atmosphere of some localities is also conducive to corrosion.

Painting the equipment to prevent its deterioration is often resorted to, but this is not entirely satisfactory, since corrosion occurs at breaks in the paint film and serious damage to the metal parts may result before it is visible to one inspecting the setup. There are also parts which it is not feasible to paint, such as the interior of the pipes or other inaccessible parts.

A brief outline of the operation of an air-conditioning system may assist the reader in understanding the corrosive conditions encountered therein. For operation during the summer, it is necessary to cool and dehumidify the air as it is drawn from the outside. This is accomplished by blowing the incoming air through a spray of refrigerated

water. By this treatment most of the dust particles and certain gases that are present are removed. The gases, sulfur dioxide and carbon dioxide, in uniting with the water form sulfurous acid and carbonic acid. The former, on oxidation, yields sulfuric acid. In air-conditioning systems it is not economical to use fresh water continuously. After leaving the sprays, the water flows to a recirculating pump and is pumped back to the cooling system and thence to the sprays, and the cycle is repeated. Thus the contaminating impurities in the air are continually being built up in the wash water, and at the same time the pH of the water decreases rapidly, unless some alkaline substance is added to neutralize the acid that is formed. In winter operation, the cycle is the same, except that refrigeration of the spray water is omitted.

II. SCOPE OF THE INVESTIGATION

Two possible methods of reducing the losses from corrosion suggest themselves. One of these is the careful selection of the materials of construction to secure maximum resistance to corrosion, the other is the treatment of the water by the addition of suitable chemicals which will inhibit the corrosive attack. The present investigation was directed toward a study of the latter phase of the subject.

It has been known for many years that certain chemicals, when added to water even in small amounts, will retard corrosion of iron immersed therein. The usual explanation for this is that the chemical produces a film on the surface of the iron which prevents the corrosion reaction from proceeding.

None of the ready-made mixtures sold commercially as inhibitors was used in this work nor was any attempt made to simulate commercial inhibitors by making up mixtures of this kind. Instead, the chemicals which form the basis of such inhibitors were used. These chemicals were (1) sodium dichromate, (2) sodium silicate, (3) sodium phosphate, and (4) sodium carbonate.

The concentration of each of the chemicals was varied from 100 to 500 ppm.

The pH in most of the runs was maintained between 8.0 and 9.0, but the effect of drop in the pH to between 4.0 and 5.0 was studied in two of the runs made.

The effect on the inhibiting action of the pick-up of sulfates and chlorides, such as results from the absorption of impurities in the air, was included in the study.

In order to answer the question which may be raised as to whether the effectiveness of an inhibiting treatment varies with the conditions under which the corrosive attack occurs, the tests were carried out in several ways. Some of the specimens were tested by immersion in a stream of the treated water flowing at a constant rate of 5 ft./min. Others were tested with a fine spray of the treated water impinging directly on their surfaces. It is well known that corrosion within a crevice opening out to the surface is usually more severe than the attack on a relatively plane surface of the same specimen. To determine the effectiveness of the inhibiting treatment against "crevice corrosion," some of the test specimens consisted of an assembly of two simpler ones, so as to simulate a crevice. These were subjected to corrosion by simple immersion as well as by spraying.

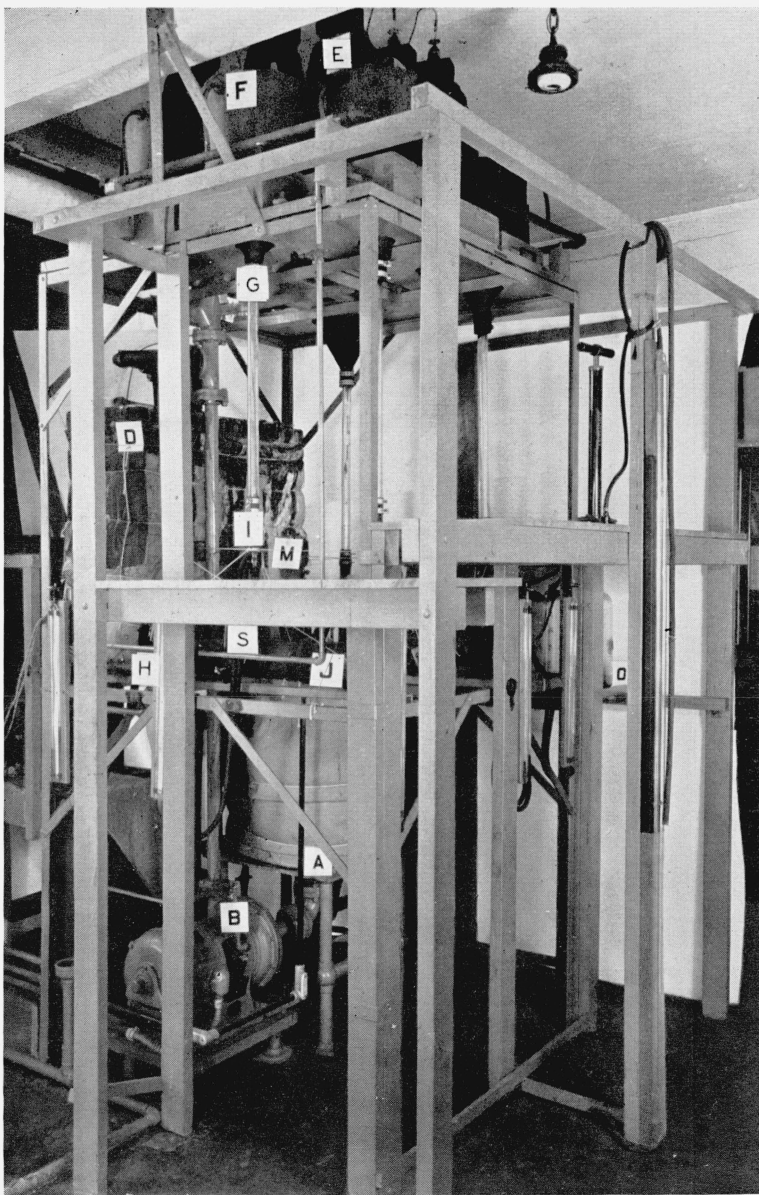


FIGURE 1.—Apparatus used in the investigation.

A, lower tank; B, pump; C, upper tank; D, spray chamber; E, siphon; F, header; G, glass tube; H, manometer for flow-meter; I, orifice; J, valve; K, pressure gage; L, holder for spray specimens; S, screw clamp, V_1 and V_2 , valves.

Six ferrous sheet materials were used throughout the test. These materials were (1) a copper-bearing steel, (2) an open-hearth iron, (3) an alloyed open-hearth iron, (4) a low-alloy steel, (5) a wrought iron of the new "synthetic" type, and (6) a hand-puddled wrought iron. The results illustrated in figure 4, upon which conclusions were drawn as to the relative merits of the inhibitors used, are the averages for all materials. Although some differences in the behavior of the various materials were observed, they were not considered great or consistent enough to constitute a significant factor affecting these conclusions.

III. APPARATUS

The apparatus used in this investigation is shown in figure 1, and the action is shown diagrammatically in figure 2. The apparatus is

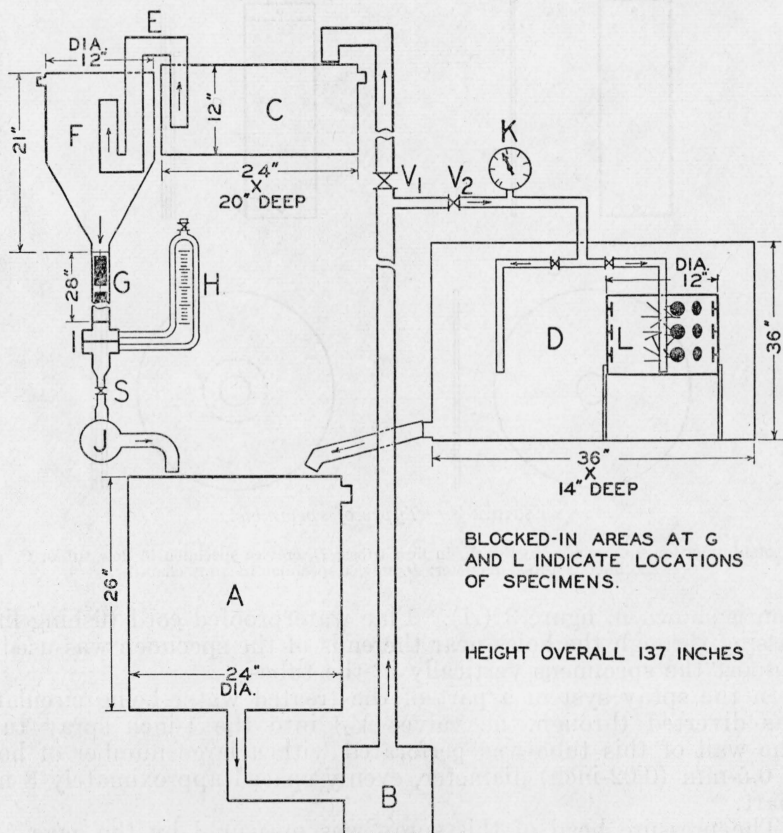


FIGURE 2.—Diagram of the corrosion apparatus.
(Significance of letters is the same as in figure 1)

similar in many respects to that used by Rawdon and Waldron.¹ All parts of the apparatus were constructed of hard rubber, with the exception of the flow tubes, which were of Pyrex glass. This made

¹ H. S. Rawdon and L. J. Waldron, *Continuous-flow corrosion tests of steel pipe*. Proc. Am. Soc. Testing Materials, 35, pt. 2, 233 (1935).

certain that no other metal except those being tested could come in contact with the treated water. The total liquid capacity of the apparatus was approximately 115 gallons.

The course of the liquid through the apparatus is indicated by arrows in figure 2. In conducting the test run, the solution was pumped from the lower tank (A) to the upper tank (C) by the acid-resisting rubber-lined pump (B). From here it was siphoned into a group of headers (F) and allowed to flow by gravity down the tubes (G) in which the specimens were suspended, and from here the liquid returned to the lower tank and the cycle was repeated. The rate of flow was regulated by the screw clamp (S) and was measured by the flow meter (H). The specimens used in this part of the test were 3- by 1-inch rectangles cut from 19-gage sheet. This type of speci-

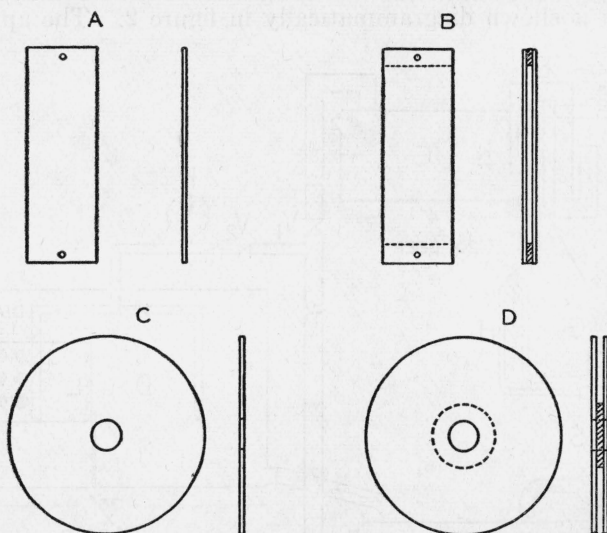


FIGURE 3.—Types of specimens.

A, total-immersion specimen, 1- by 3-inch, in flow tubes; B, crevice specimen in flow tubes; C, spray specimen, $2\frac{3}{4}$ -inch diameter; D, crevice specimen in spray chamber.

men is shown in figure 3 (A). Fine waterproofed cord (fishing line) passing through the holes near the ends of the specimen was used to support the specimens vertically in the tubes.

In the spray system a part of the treated water being circulated was diverted through the valve (V_2) into the 1-inch spray tube. The wall of this tube was perforated with a large number of holes of 0.5-mm (0.02-inch) diameter, evenly spaced approximately 8 mm apart.

The pressure head of this spray was measured by the gage (K). The force of the spray was kept constant by maintaining a pressure of 9 lb/in.² The spray specimens were supported in a hard-rubber cylindrical holder encircling the spray tube. This holder, 12 inches in diameter and 10 inches high, accommodated three rows of specimens, 10 in each row. Each specimen, $2\frac{3}{4}$ inches in diameter with a $\frac{3}{8}$ -inch central hole (fig. 3, C), was mounted on a hard-rubber rod

about 1 inch long and $\frac{5}{8}$ inch in diameter which had been turned down to $\frac{3}{8}$ inch in diameter on one end for a distance of about $\frac{3}{8}$ inch and threaded. The threaded end was inserted through the hole so as to hold the specimen securely against the shoulder of the rod when a hard-rubber nut of $\frac{5}{8}$ -inch outside diameter was screwed on to the rod. This rod, carrying the specimen, was then screwed into the holder.

The lower tank was provided with an immersion electric heater and temperature regulator for maintaining a constant temperature of $35^{\circ}\text{C} \pm 0.2^{\circ}$.

IV. PROCEDURE

A preliminary study was made of the method of preparing the surfaces of the specimens prior to placing them in the apparatus. Wet surface grinding gave results which could be repeated most closely.

The following procedure was therefore adopted in the preparation of the specimens:

1. Both sides were ground on the surface grinder, using a 3860-H8B Norton wheel, and care being taken to remove all the mill scale.

2. The specimens were degreased with trichloroethylene in a vapor degreaser.

3. They were then weighed on an analytical balance.

4. The backs of those specimens of which only one surface was to be exposed to the liquid were coated with a mixture of gutta-percha and ozokerite wax in approximate proportions, 1:2. These specimens included those in the spray test and those in which the effect of a crevice was being studied.

5. The types of specimens to be used for studying crevice corrosion were assembled so that the bare surfaces faced each other as shown in figure 3(B) and 3(D). Type B was used for the totally immersed samples and type D for those in the spray. The specimens were separated by means of waxed-paper or waxed-cloth spacers, the width of the resulting crevice being approximately 0.03 inch. This was measured by means of a feeler gage.

All specimens were placed in the apparatus as previously described, and, at the end of the run of 14 days' duration, were removed and photographed. The rust was then removed electrolytically by making the specimens the cathode in a 10-percent ammonium-citrate solution, carbon anodes and a current density of 2 or 3 amp/dm² being used. After washing and drying, the specimens were again weighed and the loss was calculated in grams per square decimeter for a period of 14 days.

A blank to determine the loss produced by the cathodic cleaning operations was run for each of the materials tested. The loss was found to be nearly negligible, if the procedure described was followed and all mill scale was removed before starting. However, if this were not done, this cleaning removed the oxides in the scale. The measured losses in certain cases amounted to several times the actual corrosion loss.

The solutions were prepared by dissolving a weighed amount of the appropriate chemical in Washington city water. In many of the preliminary tests, distilled water was used in making up the solutions. The differences in the results obtained in the two cases were not considered significant. In actual practice, tap water is always used.

The results² of an average analysis of the raw water used in this investigation are as follows:

Silica.....	2 ppm.
Calcium.....	27 ppm.
Magnesium.....	3 ppm.
Chloride.....	6 ppm.
Sulfate.....	30 ppm.
Bicarbonate.....	60 ppm.

The amount of chemical added was calculated to correspond in concentration to the anhydrous salts, $\text{Na}_2\text{Cr}_2\text{O}_7$, Na_2SiO_3 , Na_3PO_4 , and Na_2CO_3 , respectively. The chemicals used in the actual preparation of the solutions are as follows:

Sodium chromate and dichromate.....	$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$.
Water glass.....	$\text{Na}_2\text{Si}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ (sodium silicate, 40° Bé solution).
Sodium metasilicate.....	$\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$.
Sodium disilicate.....	$\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.
Sodium phosphate.....	Approximately equal parts of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.
Sodium hexametaphosphate.....	$(\text{NaPO}_3)_6$.
Sodium carbonate.....	Approximately equal parts of Na_2CO_3 and NaHCO_3 .
Sulfate.....	Sulfate ions were supplied by Na_2SO_4 for pH of 8 to 9, and by H_2SO_4 for pH of 4 to 5.
Chloride.....	Chloride ions were supplied by NaCl for pH of 8 to 9, and by HCl for pH of 4 to 5.

The acidity of the solutions as they were prepared was slightly higher than that planned to be used in the test. After the chemicals had been dissolved and thoroughly mixed, the pH of the bath was adjusted to the desired value by the addition of sodium hydroxide. In order to maintain the pH at the desired value during the run, it was necessary to make small additions of sodium hydroxide for runs in which a pH of 8 to 9 was desired and of sulfuric acid for a desired pH of 4 to 5. In those cases in which the composition of the inhibiting chemical was uncertain, as in water glass, a chemical analysis of the bath served as a check on this composition, and the necessary adjustment was made accordingly.

V. RESULTS

1. TOTAL IMMERSION AND SPRAY

The compositions of the solutions used in 14 different corrosion-inhibiting treatments are given in table 1. The average loss in weight obtained in each of these water treatments is shown graphically in figure 4. The loss in weight in each case is the average of duplicate determinations for each of the six ferrous sheet materials used, with the exception of runs 2, 12, and 14, in which cases triplicate determina-

² Data supplied by C. J. Lauter, chief chemist, Dalecarlia Filter Plant, Washington, D. C.

tions were made of each material. The height of the solid blocked-in areas in figure 4 represents the loss in weight occurring in the specimens which were totally immersed in the liquid flowing at the rate of 5 linear feet per minute. The height of the cross-hatched areas represents the average loss in weight of the specimens exposed to the spray for the different runs indicated.

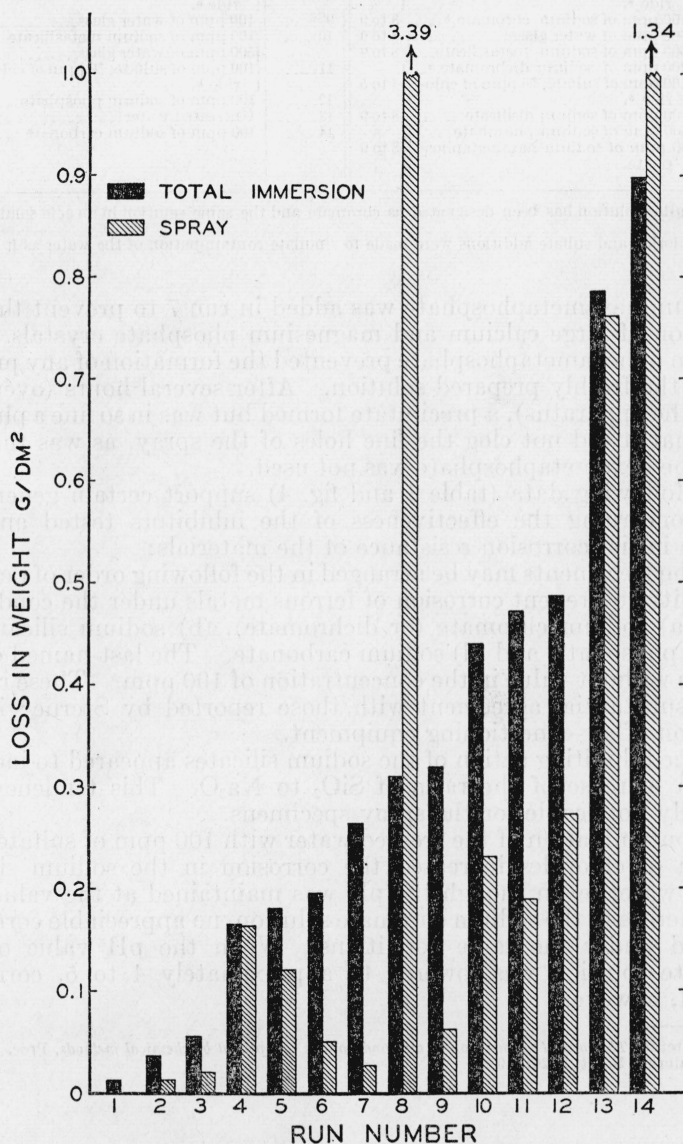


FIGURE 4.—Chart showing the average loss in weight for the period of 14 days of the six materials tested, using the water treatments listed in table 1.

TABLE 1.—Summary showing concentration of inhibitors and pH of solutions in the various water treatments used

Run No.	Concentration of inhibitor	pH	Run No.	Concentration of inhibitor	pH
1.....	{200 ppm of sodium chromate ^a 100 ppm of sulfate; 50 ppm of chlor- ide ^b}	8 to 9	8.....	{500 ppm of water glass..... 100 ppm of sulfate; 50 ppm of chlor- ide ^b}	4 to 5
2.....	100 ppm of sodium chromate ^a	8 to 9	9.....	100 ppm of water glass.....	8 to 9
3.....	500 ppm of water glass.....	8 to 9	10.....	100 ppm of sodium metasilicate.....	8 to 9
4.....	500 ppm of sodium metasilicate.....	8 to 9	11.....	{500 ppm of water glass..... 100 ppm of sulfate; 50 ppm of chlor- ide ^b}	8 to 9
5.....	{200 ppm of sodium dichromate ^a 100 ppm of sulfate; 50 ppm of chlor- ide ^b}	4 to 5	12.....	100 ppm of sodium phosphate.....	8 to 9
6.....	500 ppm of sodium disilicate.....	8 to 9	13.....	Untreated water.....	8 to 9
7.....	{500 ppm of sodium phosphate..... 50 ppm of sodium hexametaphos- phate.....}	8 to 9	14.....	100 ppm of sodium carbonate.....	8 to 9

^a An alkaline solution has been designated as chromate and the same solution in an acid solution as dichromate.

^b The chloride and sulfate additions were made to simulate contamination of the water as it occurs in service.

Sodium hexametaphosphate was added in run 7 to prevent the precipitation of large calcium and magnesium phosphate crystals. The addition of hexametaphosphate prevented the formation of any precipitate in the freshly prepared solution. After several hours (overnight run in the apparatus), a precipitate formed but was in so fine a physical state that it did not clog the fine holes of the spray, as was the case when the hexametaphosphate was not used.

The following data (table 1 and fig. 4) support certain generalizations concerning the effectiveness of the inhibitors tested and the relative initial corrosion resistance of the materials:

1. The treatments may be arranged in the following order of decreasing ability to prevent corrosion of ferrous metals under the conditions used: (a) sodium chromate (or dichromate), (b) sodium silicate, (c) sodium phosphate, and (d) sodium carbonate. The last-named chemical was without value in the concentration of 100 ppm. These results are in substantial agreement with those reported by Sterne³ in the operation of air-conditioning equipment.

2. The inhibiting action of the sodium silicates appeared to increase with an increase of the ratio of SiO_2 to Na_2O . This tendency was especially noticeable for the spray specimens.

3. Contamination of the treated water with 100 ppm of sulfates and 50 ppm of chlorides increased the corrosion in the sodium silicate treated water, even though the pH was maintained at the value of 8 to 9, whereas in the sodium chromate solution, no appreciable corrosion occurred under the same conditions. When the pH value of the chromate solution was lowered to approximately 4 to 5, corrosion resulted, however.

³ C. M. Sterne, *The control of corrosion in air conditioning equipment by chemical methods*, Proc. Am. Soc. Testing Materials 35, pt. 2, 261 (1935).

4. A striking difference in the rate of corrosion of specimens exposed in total immersion as compared with those subjected to the spray occurred in run 8, in which the inhibitor consisted of 500 ppm of water glass in a solution with a pH of 4 to 5 and contaminated by sulfate and chloride impurities. The explanation of this apparent disagreement was that under the total immersion conditions a gelatinous coating, evidently insoluble silicic acid, covered the specimens and protected them from corrosion. This coating was from $\frac{1}{16}$ to $\frac{1}{8}$ in. thick and was easily visible on the specimens. Formation of this coating was prevented on the spray specimens, so that corrosion proceeded normally.

The effect of this coating on the corrosion also accounts for the greater loss in weight of the totally immersed specimens of run 11 than of those of run 8.

However, in most of the runs, the loss in weight was greater for the specimens immersed in the slowly moving liquid than for those specimens exposed to the spray. It is thought that the reason for this difference was that the spray washed off all loose corrosion products, so that most of the surface was maintained approximately in its original condition. This action tended to keep the anodic areas at a minimum. On the other hand, in the flow tubes the motion of the liquid was so slow that the corrosion products were not removed rapidly but were slowly carried down the surface of the specimen, thereby stimulating corrosion at a point immediately below that at which it started. As this process continued, the anodic areas increased in extent. Thus, at the end of a run, the corrosion on the immersed specimens was in the form of long narrow streaks, whereas that on the spray specimens occurred at individual points on the surface as pits.

Some variation was noted in the initial corrosion resistance of the six materials used in the investigation. This variation, however, was of minor significance when compared with the variations resulting from a change in the inhibitor. In other words, corrosion was prevented from occurring on all materials under certain conditions, whereas under other conditions it took place on all the materials. No conditions were found in which corrosion was present on some of the materials and absent on others. Since the runs were of only 14 days' duration, the slight differences in loss in weight of the various materials were not sufficient to draw conclusions as to the superiority or inferiority of these materials.

2. CORROSION IN CREVICES

Corrosion is often more severe within small crevices than on flat surfaces of the same piece. Observations on the corrosion in crevices were therefore included in each run to determine whether serious corrosion might develop from this cause. The specimens were assembled as shown in figures 3 (*B* and *D*), and the results are given in table 2.

TABLE 2.—*Comparative merits of inhibitors in crevice corrosion, with an approximate width of crevice of 0.03 inch*

[Average loss of weight determined on 6 types of ferrous sheet materials in test runs of 14 days' duration, arranged in the same order as in table 1]

Run No.	Concentration of inhibitor	pH	Average loss in weight for 14 days	
			Total immersion (flow, 5 ft/min)	Spray
			mg/dm ²	mg/dm ²
1	200 ppm of sodium chromate	8 to 9	54	
2	100 ppm of sulfate; 50 ppm of chloride *			
3	100 ppm of sodium chromate	8 to 9	51	21
4	500 ppm of water glass	8 to 9	88	52
5	500 ppm of sodium metasilicate	8 to 9	133	260
6	200 ppm of sodium dichromate	4 to 5	239	109
7	100 ppm of sulfate; 50 ppm of chloride *			
8	500 ppm of sodium disilicate	8 to 9	183	125
9	500 ppm of sodium phosphate	8 to 9	63	137
10	50 ppm of sodium hexametaphosphate			
11	500 ppm of water glass	4 to 5	221	537
12	100 ppm of sulfate; 50 ppm of chloride *			
13	100 ppm of water glass	8 to 9	129	289
14	100 ppm of sodium metasilicate	8 to 9	246	323
15	500 ppm of water glass	8 to 9	150	293
16	100 ppm of sulfate; 50 ppm of chloride *			
17	100 ppm of sodium phosphate	8 to 9	327	431
18	Untreated water	8 to 9	309	730
19	100 ppm of sodium carbonate	8 to 9	262	598

* The chloride and sulfate additions were made to simulate contamination of the water as it occurs in service.

It will be observed that the order of relative merit in which the inhibitors were placed by loss in weight resulting from crevice corrosion was, with a few exceptions, similar to that in which they were placed by the simple immersion or spray tests. Some corrosion occurred in the crevices of all the specimens as compared with a practically complete absence of corrosion in the total immersion and spray specimens of runs 1 and 2. On the other hand, in those cases in which the inhibitor was not especially efficient and a comparatively large amount of corrosion normally would occur on an exposed surface, the resulting corrosion products soon filled the crevice and further corrosion was arrested.

In several of the runs the width of the crevice was varied from a few thousandths of an inch to approximately 0.05 inch. The material used in these special tests was a plain carbon steel, and a glass microscope slide was placed on each side of the specimen. It was found that the corrosion loss was approximately proportional to the width of crevice, as shown in figure 5. The corrosion occurring in these crevices started along the medial longitudinal line of the specimen, this being the most inaccessible region for the replenishment of the solution and its dissolved oxygen. However, on continuing the run, this crevice slowly became filled with corrosion products, so that the total loss was a function of the available space within the crevice. The deficiency of oxygen in the inaccessible regions of the crevice was plainly revealed by the color of the corrosion products. Greenish ferrous compounds formed at the center of the specimens, and reddish-brown ferric compounds formed along the edges where the supply of dissolved oxygen was more abundant. Some of the variation of the results given in table 2 may be attributable to nonuniformity of the width of the

crevice, despite the fact that attempts were made in most of the runs to keep this width constant. It also appears that the greatest amount of corrosion may occur with one width of crevice under one set of conditions of inhibitor, pH, etc., and a different width of crevice

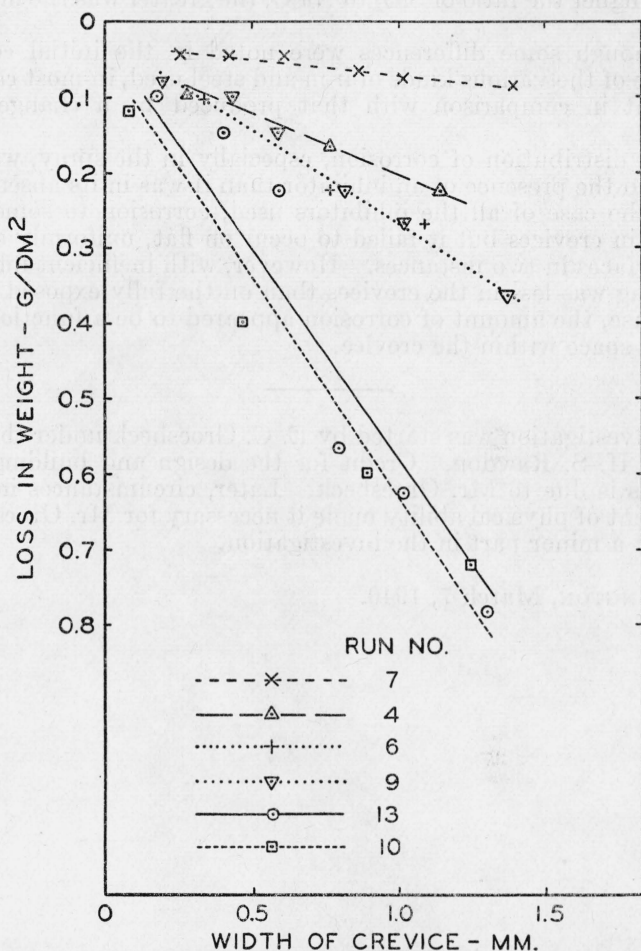


FIGURE 5.—Effect of the width of crevice on the degree of corrosion occurring therein.

The conditions for the different runs were the same as those listed in tables 1 and 2.

is conducive to the maximum corrosion under a different set of conditions.

VI. SUMMARY

This study has disclosed a number of generalizations on the corrosive properties of water which has been treated with small amounts of corrosion-inhibiting chemicals. Some of the more important of these trends are listed in the following summary:

1. All of the inhibitors tested, with the exception of 100 ppm of sodium carbonate, decreased the rusting of iron or steel.

2. The order of decreasing efficiency of the inhibitors studied in the concentrations used, was (a) chromates, (b) silicates, (c) phosphates, and (d) carbonates.

3. In the case of the sodium silicates tested, the results indicated that the higher the ratio of SiO_2 to Na_2O , the greater was the inhibiting action.

4. Although some differences were noted in the initial corrosion resistance of the various kinds of iron and steel used, in most cases this was slight in comparison with that produced by a change in the inhibitor.

5. The distribution of corrosion, especially in the spray, was more uniform in the presence of an inhibitor than it was in its absence.

6. In the case of all the inhibitors used, corrosion to some extent occurred in crevices but it failed to occur on flat, uniformly exposed, metal surfaces in two instances. However, with inefficient inhibitors, the rusting was less in the crevices than on the fully exposed surface. In this case, the amount of corrosion appeared to be a function of the available space within the crevice.

This investigation was started by E. C. Groesbeck under the supervision of H. S. Rawdon. Credit for the design and building of the apparatus is due to Mr. Groesbeck. Later, circumstances involving impairment of physical ability made it necessary for Mr. Groesbeck to take only a minor part in the investigation.

WASHINGTON, March 7, 1940.