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By

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Corrosion by Water at Low Flow Velocity

By *T. E. Larson and R. M. King*

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UP to the present there has apparently been no organized program for studying corrosion by fresh water. No pattern has been established even to define a corrosive water under various conditions of use.

The saturation index *(1, 2)* for calcium carbonate has been devised and applied with the intent of providing a thin, controlled scale or film of calcium carbonate on the metal surface, thereby reducing or preventing corrosion. The saturation index indicates the tendency toward, but not the rate of, deposition or solution of calcium carbonate in a water, and does not necessarily show corrosivity, a fact that many water works chemists have long recognized.

The current practice appears to be either: [1] to assume that a water is corrosive and to treat it whether necessary or not; or [2] to assume that it is not corrosive until "red water" troubles develop or equipment failure is experienced, and then to apply the corrective treatment that seems most likely to succeed.

In 1924 Whitman, Russell, and Altieri (J) concluded from careful experiments with Cambridge, Mass., water that, in the pH range 4.1-10 at 22°C and 4.3-9 at 40°C, hydrogen ion concentration has no effect on the rate of corrosion, and the main variable in this pH region is the rate at which dissolved oxygen diffuses to the metal surface. This conclusion was not intended to apply to waters of other mineral character, but it has been variously misquoted or enlarged upon to imply that dissolved oxygen controls the rate of corrosion in natural waters. The latter interpretation of the Cambridge results was proved incorrect by Baylis *(4)* in 1926. He demonstrated the practical value of calcium carbonate protection by controlled pH and the low solubility of ferrous carbonate at a pH greater than 8.

Because, in reality, each addition of caustic or acid to adjust the pH of Cambridge water produced a water of different mineral quality, the conclusions reached by Whitman and his colleagues need not be applicable to water of the same mineral quality as that at Cambridge or to potable waters in general.

Long experience has taught water works personnel the value of pH control for corrosion protection, but it has also shown that factors other than pH and dissolved oxygen influence corrosion rates. Data available in the form of mineral analyses have not been amenable to interpretation owing to the lack of experimental evaluation.

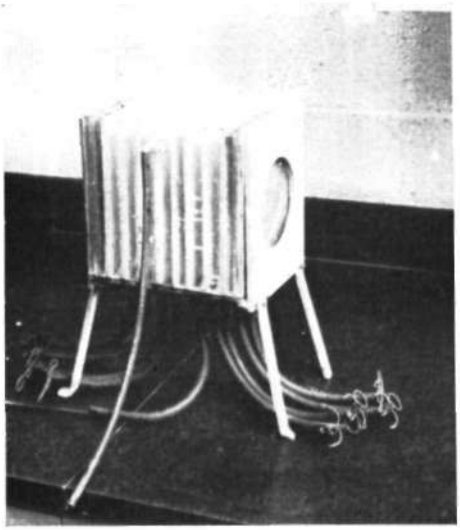

Fig. 1. Experimental Corrosion Cell

The electrolysis cell is divided into nine compartments by alundum plates between the two iron electrodes.

It is the purpose of this paper to demonstrate that water quality is a primary factor in corrosion (specifically at low flow velocities) and that the influence of dissolved oxygen and pH on corrosion rates is secondary. It is believed that the data presented will provide a basis for comparison with information obtained in future studies and in practical experience.

Qualitative Studies on Ion Migration

An elementary investigation was begun in 1948, with the assistance of John Grench of the Illinois Water Survey Div., to obtain qualitative data on the water composition at the cathode and the anode, as affected by waters of different mineral composition. The investigation was designed to study the general water quality conditions that develop between two iron electrodes under the influence of an artificially impressed voltage to produce a current density of a limited magnitude. The electrodes were located at opposite ends of an electrolysis cell divided into nine 470-ml compartments by vertical, parallel porous alundum plates (Fig. 1). University of Illinois

TABLE 1

Tap Water Composition

Item		Amount	
		ppm	*epm**
Iron	(Fe)	trace	
Manganese	(Mn)	trace	
Calcium	(Ca)	60.0	3.0
Magnesium	(Mg)	24.0	2.0
Sodium	(Na)	46.0	2.0
Silica	(SiO_2)	19.0	
Fluoride	(F)	0.3	
Chloride	(Cl)	6.0	0.20
Nitrate	(NO_3)	0.2	
Sulfate	(SO_4)	9.6	0.20
Alkalinity (as $CaCO_3$)		330.0	6.60
Hardness (as $CaCO_3$)		250.0	5.00
Dissolved oxygen		6.0	
Temperature		55° F	
pH		7.4	

* Equivalents per million.

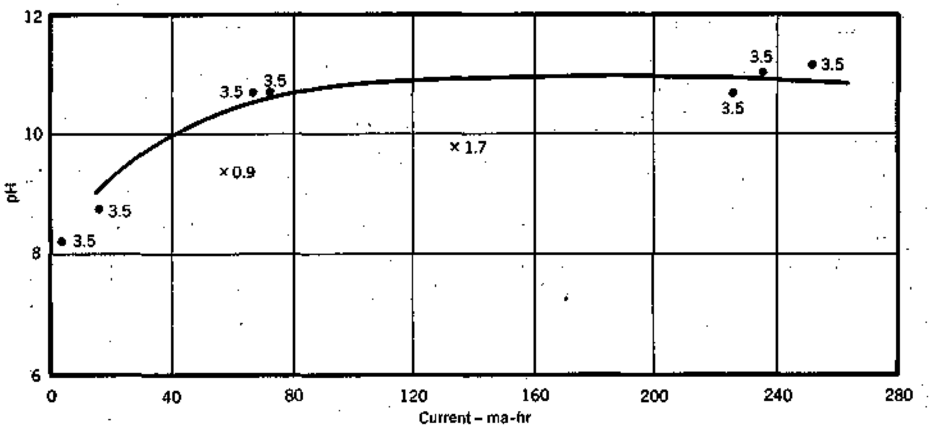

Fig. 2. pH at Cathode

The numbers at scattered points represent the current density in milliamperes per square foot.

tap water was permitted to flow through the center compartment at a rate of 300 ml per minute, while,' in the remaining compartments, the water was in a quasi-stagnant condition. No attempt was made to aerate the water or to exclude dissolved oxygen. The composition of the water is indicated in Table 1.

Progressive quality changes occurred in each compartment with increasing milliampere-hours of current consumption. The changes were particularly significant in the end compartments. The increase in pH at the cathode is shown in Fig. 2, and the accompanying reduction in calcium and magnesium in Fig. 3 and 4. It will be noted that, at low current density, the pH was not affected so greatly for equivalent milliampere-hour values, and, accordingly, magnesium precipita-

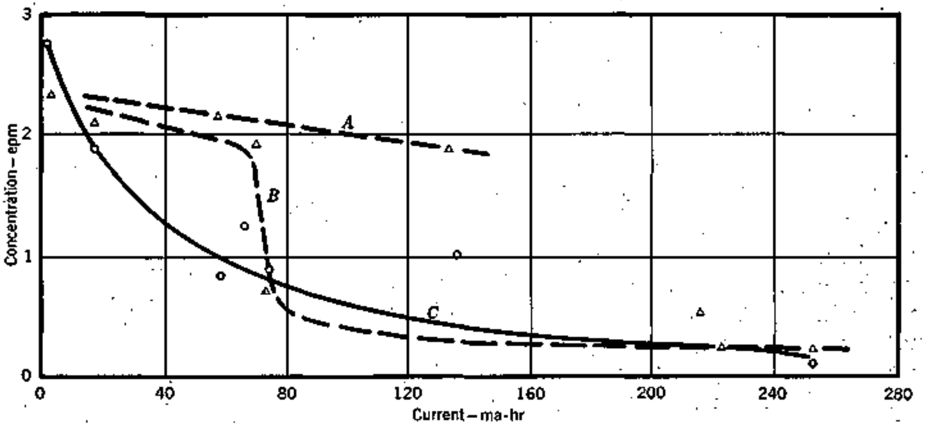

Fig. 3. Magnesium and Calcium Concentration

Key: A—*magnesium, low current density (0.9-1.7) ma per square foot);* B—*magnesium, high current density (3.5 ma per square foot);* C—*calcium.*

tion did not occur during these tests.

The general distribution of calcium, magnesium, and alkalinity concentrations in the various compartments is shown in Fig. 5. The repeated loss of alkalinity toward the anode compartment was noteworthy.

In several tests, measurements were made on polyphosphate and silica concentrations in each of the compartments. When polyphosphate or silica was present originally in all the compartments, these tests showed a progressive decrease in the concentration of these ingredients in the compartments near the anode and the cathode. When all but the center compartments were free from polyphosphate, however, the migration of polyphosphate was definitely toward the cathode at low current density (0.4 ma per square foot), while, at high current density (4 ma per square foot), polyphosphate was found to migrate toward anode and cathode at equal rates.

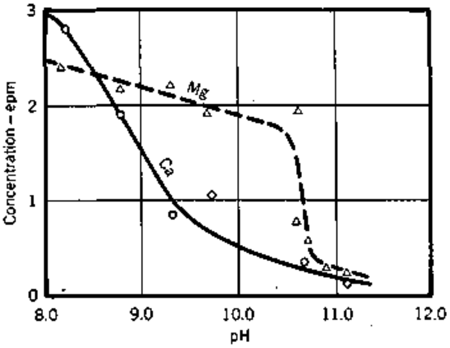

Fig. 4. Concentrations at Cathode

The curves show the concentrations of calcium and magnesium in the compartment adjacent to the cathode.

It would have been interesting to continue these tests with water containing bicarbonate and more chloride, but it was decided to use a different

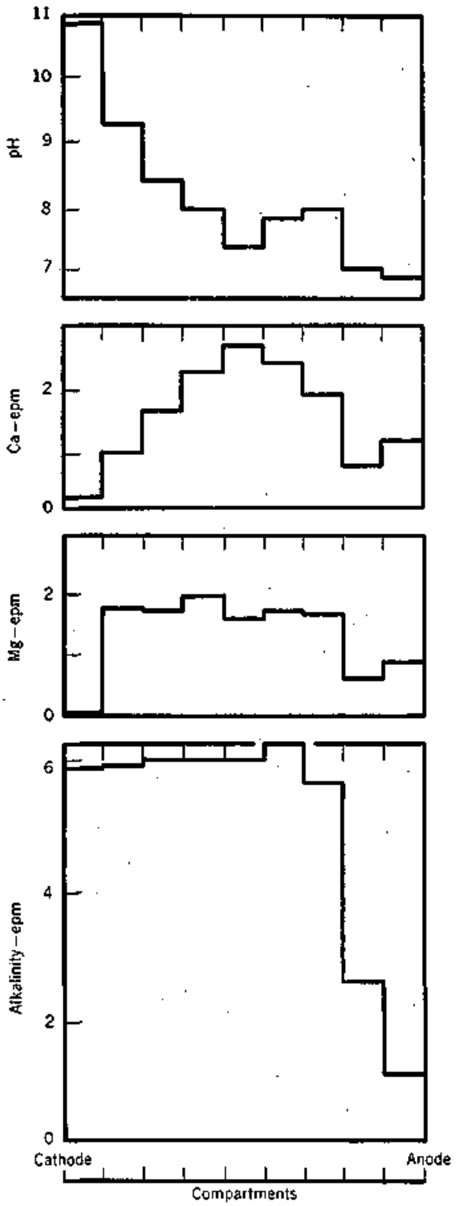

Fig. 5. Concentrations in Compartments

The curves show the concentrations (in equivalent parts per million) of alkalinity, magnesium, and calcium, as well as the pH, in the various compartments.

approach to study the influence of bicarbonate and carbonate ions on corrosion rates.

Immersion Tests

As all natural waters contain bicarbonates in at least a small concentration, it was felt that consideration should be given to different proportions of bicarbonate and other anions in corrosion tests with controlled synthetic solutions containing known concentrations of sodium salts, eliminating the possible added influence of bivalent metal ions. Borgmann (5) has indicated the relative corrosiveness of salts of numerous cations and anions, exclusive of bicarbonate and carbonate and largely in concentrations greater than that in natural waters.

The effect of carbonate ions as an inhibitor of corrosion was previously demonstrated by Evans *(6)* in 1927. Mears and Evans (7), in 1935, described in detail the inhibiting effect of potassium carbonate on solutions containing potassium chloride. These data, however, concerned strips of steel partially immersed in solutions of known concentrations, and provided no information on the pH of the resultant mixtures of carbonate and chloride salts. In other words, although the potassium carbonate concentration varied, the pH was not held constant and it also varied for the various proportions. Therefore, both pH and carbonate ion variables affected the results.

Apparatus of the standard type *(8)* for total-immersion tests of nonferrous metals was constructed for the studies (Fig. 6). The 1½ × 3-in. specimens of 0.01-in. "black plate" steel (free from mill scale) that were used were reported to have the following composition (by percentage): C, 0.07; Mn, 0.30-0.45; P, 0.015 maximum; S, 0.050 maximum; and Si, 0.010 maximum.

The specimens were degreased in carbon tetrachloride; placed in a 5 per cent solution of HCl and HNO_3 for 2 min; placed in concentrated HCl for 1 min; rinsed in acetone; and dried and weighed 48 hr before use. The edges were coated with paraffin, and a scratch was made on both sides of the specimen just prior to immersion in 18 liters of water for a 3-day test at a flow velocity of 0.085 fps at room temperature. A low velocity was deliberately chosen in order to simulate the conditions usually existing in as much as 25-50 per cent of any municipal distribution system, including the service lines.

Fig. 6. Total-Immersion Test Setup

The specimens used were of black plate steel, free from mill scale. The apparatus was of standard type.

Various proportions of sodium bicarbonate and chloride were used at pH 7 and 9. Likewise, various proportions of sodium bicarbonate and sulfate were used at these pH values, and various proportions of sodium bicarbonate and nitrate were used at pH 7. Carbon dioxide was employed to control pH. The results are shown in Fig. 7.

Discussion of Results

It was noted that, after the proportion of sodium chloride or sulfate reached a given value, the corrosion rate was not influenced by further addition of these chemicals. Also, the rate was of the same order of magnitude whether chloride or sulfate was used: The corrosion rates with these proportions were therefore assumed to be governed strictly by the dissolved-oxygen content of the water. In other words, if 15 or 20 ppm dissolved oxygen was present, the corrosion rate in this range may have risen, particularly with increasing proportions of sodium chloride.

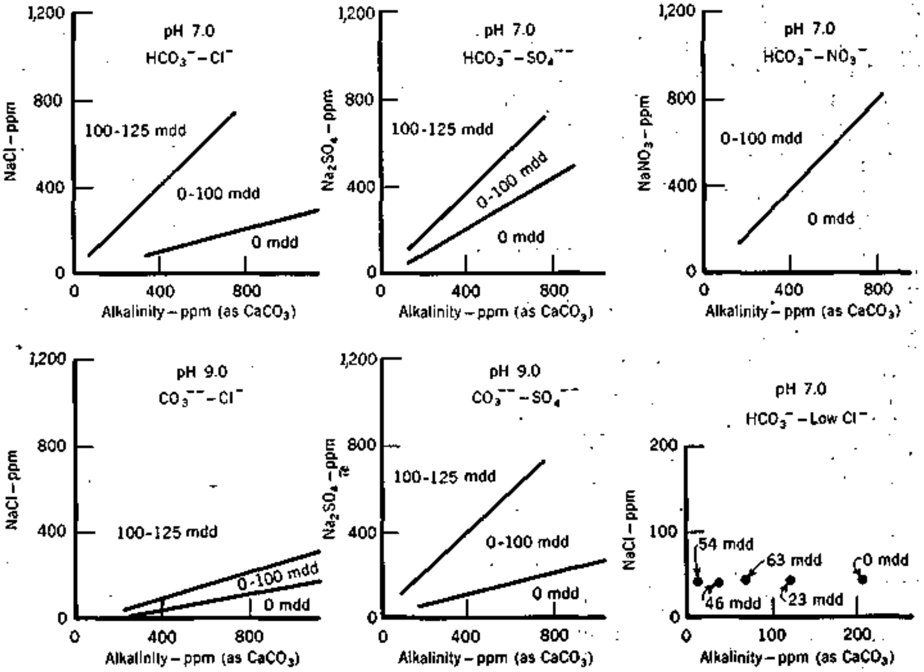

Fig. 7. Results of Total-Immersion Tests

The experiments were conducted at room temperature and constant flow velocity (0.085 fps); the dissolved-oxygen content was 8 ppm. The solid lines represent boundaries of sectors in which the corrosion rates were as shown.

It was repeatedly found that the corrosion rate was zero when a particular minimum of alkalinity was present in each test. It was also noted that an intermediate range of corrosion existed in which the rate was unpredictable under the experimental conditions. For example, of three specimens in a solution in this range, one may have corroded at a rate of 10 mg per square decimeter per day (mdd), while the two others may have corroded at a rate of 90 mdd in the same solution. In this range of water quality, the corrosion rate may have been inhibited or intensified, depending upon the extent and location of the corroded area of the specimen.

It was significant that, for any specific chloride concentration,. corrosion rates might be considerably greater for solutions of low mineral content than for those of high mineral content, a finding that is contrary to the usual predictions. It may be concluded that corrosion rates are controlled more by the specific mineral quality than by the total mineral content.

It was also significant that, for some chemical compositions, corrosion rates appeared to be greater at pH 9 than at pH *7*, while, for the others, the rates were unchanged. This also is contrary to the normal predictions on the corrosive tendency of water.

The relatively lower corrosion rates experienced with nitrates was surprising. Although a water that contains only bicarbonate and nitrate is a rarity, it should be of interest to make a further study of the effect of small concentrations of nitrate on corrosion rates in water containing various mixtures of chloride and bicarbonate.

Several spot tests with a 9-day immersion period yielded results no different from the 3-day data.

These data are specifically limited to dissolved-solids concentrations between 200 and 1,200 ppm, under the flow velocity and temperature conditions'indicated. Figure *7*, however, shows the corrosion rates experienced in a test series in which the combined sodium chloride and bicarbonate concentrations ranged from 60 to 210 ppm. Here again, it was; noted that the bicarbonate exerted an inhibitive effect. In one group of tests with University of Illinois tap water at pH 7 (— 0.4 saturation index), no corrosion was noted until 60 ppm NaCl was present.

Extreme caution is needed in interpreting these data or applying i the conclusions to other conditions.- Consideration must.be given'to the. fact that, at the low velocities employed in these studies, the electrical migration of ions under, the corrosion cell potentials plays a more important part in the process than the relatively slow diffusion rate of the dissolved oxygen. At a higher velocity, it might be expected that oxygen diffusion rates would be the more important factor. Also, the relatively high mineral content minimizes the effect of pH because the hydrogen and hydroxyl ion concentrations are relatively low. , .

One severe criticism of these data is that no attempt was made to distinguish between general corrosion and pitting. Where pitting occurs, the rate of penetration may be quite high, although the corrosion per square decimeter of the total surface may be no greater than in areas where general corrosion is experienced. Mears and Evans (7), however, have shown that pitting is less likely to occur where little or no anodic inhibitor is present.

The data obtained in the study under discussion appear to be particularly significant as a: starting point or basis of comparison for future studies. Such investigations! might involve lower quantities of dissolved oxygen, higher flow velocities, different temperatures, polyphosphates, silicates, free or combined chlorine, and even calcium at concentrations approaching or exceeding its solubility as calcium carbonate.

Inhibition by Bicarbonate and Carbonate

Normally it is contended that, in air-saturated solutions which do not corrode, the dissolved oxygen has been responsible for the formation of an invisible oxide film. Evans (9) cites many studies with electron diffraction and X-ray techniques which indicate films of ferric oxide. In fact, steel treated with pure oxygen for a sufficiently long period under proper conditions remains corrosion resistant until the film is broken or attacked.

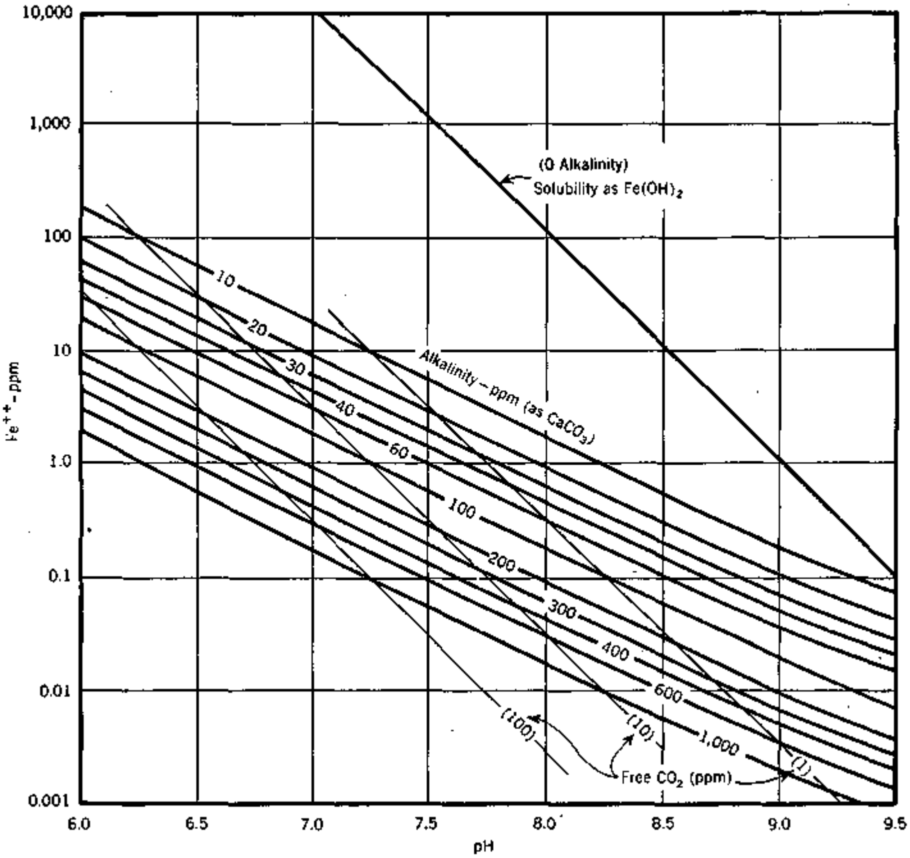

Fig. 8. Solubility of Ferrous Ion

The solubility of $FeCO_3$ *(solubility product,* 2.11×10^{-11}*) is considerably less than that of ferrous hydroxide in natural waters.*

It has often been stated that the corrosion product adjacent to the metal is ferrous hydroxide. It is extremely doubtful that this assertion holds true when carbonate or bicarbonate ions are present. Although the ferrous hydroxide theory may be perfectly correct when dealing with corrosion products derived from solutions of sodium chloride, the actual initial corrosion product' is soluble ferrous chloride, hydrolyzed insoluble ferrous hydroxide being secondary.

It will be noted in Fig. 8, however, that the solubility of ferrous carbonate is considerably less than that of ferrous hydroxide, although it is obviously greater than that of ferric hydroxide.

This appears to indicate that any inconsistency in an oxide coating would be protected immediately by ferrous carbonate rather than ferrous hydroxide.

Reconsidering the data that showed greater corrosion rates at pH 9 than at pH 7 for the same mineral quality—and accepting the assumption that ferrous carbonate provides an inhibitory film—the increased corrosion rates at pH 9 can be explained by the fact that ferrous hydroxide is more readily formed at the higher pH and is also more readily oxidized. Such localized precipitates adhering to the metal provide a physical barrier to oxygen diffusion and permit the metal surface underlying them to become anodic to the exposed surface. When sufficient alkalinity (not OH") is present, however, the flaws in an oxide coating are protected by ferrous carbonate before the ferrous ion concentration can become large enough to form ferrous hydroxide. The relative structure of ferrous carbonate and ferrous hydroxide and their reactive properties with dissolved oxygen are beyond the scope of this paper.

Summary

1. There is need for fresh-water corrosion research.
2. The experiments described demonstrate the behavior of solutions at corrosion cell electrodes.
3. Basic data have been obtained to which other data can be related in order to provide an organized approach to the water corrosion problem. Natural waters contain a corrosion inhibitor, varying in concentration or proportion from one supply to another. Without basic data on the primary, partial, or total inhibition of this natural ingredient, there is no hope of correlating the observations made on the effectiveness of other inhibitors or methods of treatment against corrosion.
4. A possible explanation has been provided for the inhibitory effect of bicarbonate and carbonate alkalinity.

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