

ISWS
C
71
Loan c.1

Circular 71

STATE OF ILLINOIS
WILLIAM G. STRATTON, *Governor*
DEPARTMENT OF REGISTRATION AND EDUCATION
VERA M. BINKS, *Director*



*Laboratory Studies Relating
Mineral Quality of Water to
Corrosion of Steel and Cast Iron*

by T. E. LARSON AND R. V. SKOLD

ILLINOIS STATE WATER SURVEY LIBRARY COPY


ILLINOIS STATE WATER SURVEY

WILLIAM C. ACKERMANN, *Chief*

URBANA

1958

Printed by authority of the State of Illinois

 14
(S6838—10-58)

Laboratory Studies Relating Mineral Quality of Water To Corrosion of Steel and Cast Iron*

By J. E. LARSON and R. V. SKOLD

Introduction

A STUDY of the effects of methods of water purification on loss in carrying capacity of water mains was begun in 1954 by the Illinois State Water Survey. Such a study was important in view of the fact that carrying capacity of water mains can be greatly reduced by obstructions to flow of water.

Obstructions in water mains may be due to: (1) the accumulation of debris, such as settled turbidity or suspended matter, (2) biological slimes or growths on the pipe walls, (3) after-precipitation of minerals left in a supersaturated state from the treatment, or (4) tuberculation (i.e., growths or the accumulation of corrosion products on the pipe wall.)

A major concern in this study of treatment methods has been to determine modifications in water quality which may cause or prevent tuberculation. Since tuberculation is a by-product of corrosion, laboratory studies were devoted to the study of mineral quality of water as related to corrosion. The type of water studied approximates the quality of Great Lakes waters.

Steel

The accelerative effect of chlorides and sulfates in causing corrosion is well known. Previous studies¹ by the Water Survey also have indicated that, even in the absence of calcium, bicarbonates inhibit the corrosion of steel. Furthermore, the proportion of the naturally occurring bicarbonate inhibitor to the chloride and sulfate in domestic waters appears to be a fundamental factor in the corrosivity of waters at pH 7 to 8 (Figure 1).

It was found that in chloride/alkalinity ratios of 0.2 to 0.4, the specimens were very sensitive to other alterations

* Submitted for publication November 7, 1957. A paper presented at a meeting of the North Central Region, National Association of Corrosion Engineers, Chicago, Illinois, October 2, 1967.

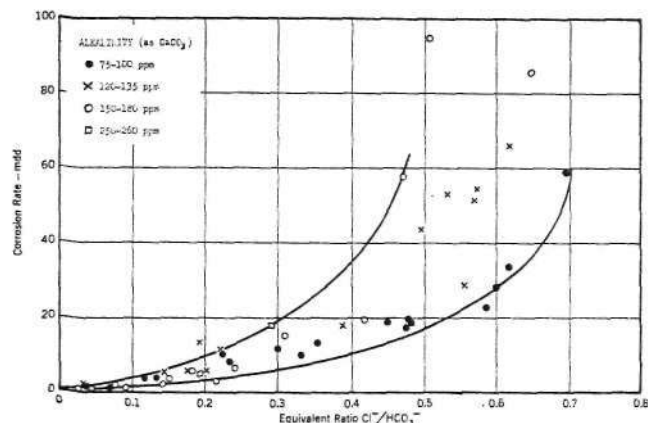


Figure 1—Effect of Cl-/HCO₃⁻ ratio of corrosion of mild steel. Alkalinity is shown as CaCO₃.

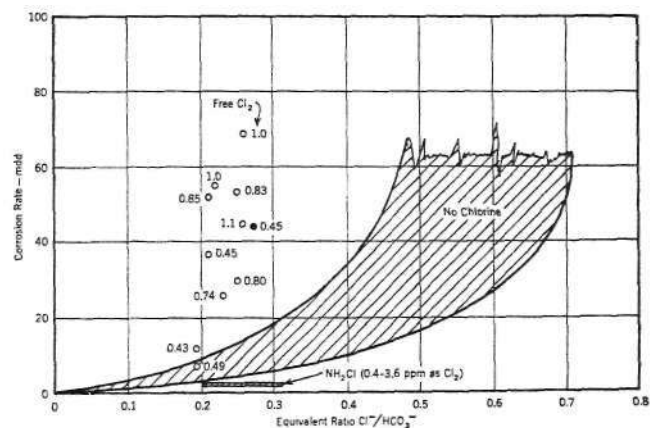


Figure 2—Effect of Cl-/HCO₃⁻ ratio on corrosion of mild steel.



Larson

Skold

THURSTON E. LARSON—Head of the Chemistry Section of the Illinois State Water Survey. He has been employed by the Water Survey since 1932 when he received a BS in chemical engineering from the University of Illinois. In 1937 he received a PhD degree. Dr. Larson has written a number of papers dealing with the subject of water quality and treatment. He is chairman of NACE Technical Unit Committee T-4E and is active in American Water Works Association committee work. He has been secretary of the Water Sewage and Sanitation Chemistry Division of the American Chemical Society for five years, serving as chairman in 1954. He is a member of AAAS and Sigma Xi.

RONALD V. SKOLD—Research Associate, Illinois State Water Survey, Urbana, Illinois. Since 1954 he has been engaged in research studies of the corrosion of water distribution lines. Mr. Skold received a BS in chemical engineering from the University of Illinois in 1949. From 1949 to 1952 he was employed at Mellon Institute where he did research in the field of adsorption. From 1952 to 1954 he was with Dearborn Chemical Company and Aquatic Inc., where he specialized in applications of ion exchange.

in quality. The presence of free chlorine was found to increase the corrosion rate of steel at chloride/alkalinity ratios of 0.2 to 0.3 (Figure 2).

A method of determining the instantaneous corrosion rate² of specimens was

Abstract

The influence of combinations of various normal mineral components in domestic waters on the rate of corrosion of cast iron and steel and on the development of tuberculation is reported. Tests were conducted with air saturated waters at room temperature with velocities of 0.1-1.0 fps and with pH controlled by carbon dioxide. The ions considered are chloride, sulfate, bicarbonate and calcium at pH 6.8-8.3. 4.6.6

developed. This method consists of determining the polarization which occurs at extremely low magnitudes of current density and of empirically relating this parameter to weight loss determinations. The authors have been extremely gratified to see the academic confirmation of this relationship by Stern³ in recent publications.

It should be mentioned also that these data were obtained with specimens totally immersed in 18 liters of prepared solutions, saturated with air at room temperature and with CO₂ used to control pH. The apparatus⁴ provided a constant velocity of the specimens in a vertical circular path. Velocities above 0.9 fps were not used. The effect of pH on corrosion (or lack of corrosion) of steel by bicarbonate waters in the absence of calcium was also determined² (Figure 3). This effect was found to be contrary to the previously accepted concept⁵ of the effect of pH. The point to be emphasized is that these data apply only to water of specific quality tested and to the conditions of the test. If the corrosive environment is altered, another relationship may occur.

Figure 4 shows results of a more recent test with a water having a much higher chloride content than that shown in Figure 3. The general trend of the data in both of these figures is similar; however, the corrosion rates in water having high chloride content are considerably higher than those in water of low chloride content. Both of these tests were conducted at low velocities.

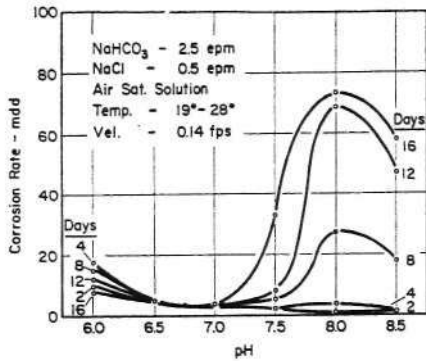


Figure 3—Effect of pH on corrosion rate of steel with $\text{Cl}^-/\text{HCO}_3^- = 0.2$

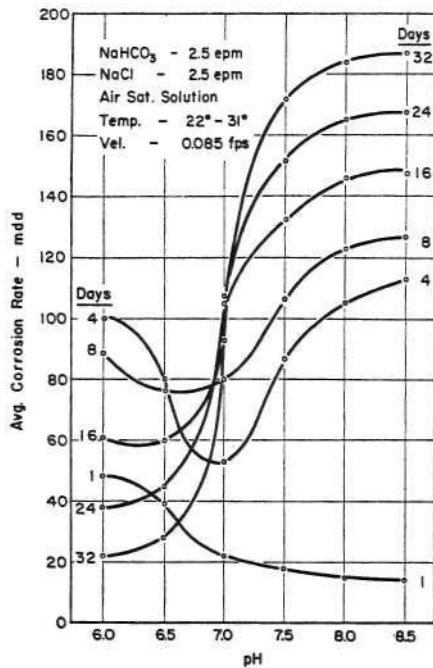


Figure 4—Effect of pH on corrosion rate with $\text{Cl}^-/\text{HCO}_3^- = 1.0$

For this particular pair of graphs, it also should be recognized that the alkalinity was constant at all values of pH. The Whitman, Russell and Altieri⁵ data were obtained with different concentrations of alkalinity and chloride at each pH. Figure 5 shows the type of corrosion products adhering to the steel specimens used to obtain the data in Figure 4. These pictures were taken at the end of the test (35 days), and the corrosion rates shown were final measured rates. It is interesting to note the increasing degree of tuberculation as the pH increases.

In the presence of calcium, as might be expected, the corrosion of steel decreased with increasing calcium concentration or with increasing pH at a chloride/alkalinity ratio of 0.4.

Cast Iron

The susceptibility of cast iron to corrosion is unlike steel. Cast iron contains graphite in a matrix of ferrite or pearlite and therefore is susceptible to initial galvanic corrosion at each graphite exposure which occurs at approximately 0.04 mm intervals.

Modern production of cast iron pipe produces an outside surface primarily of iron oxide which serves as an excellent barrier to atmospheric corrosion.

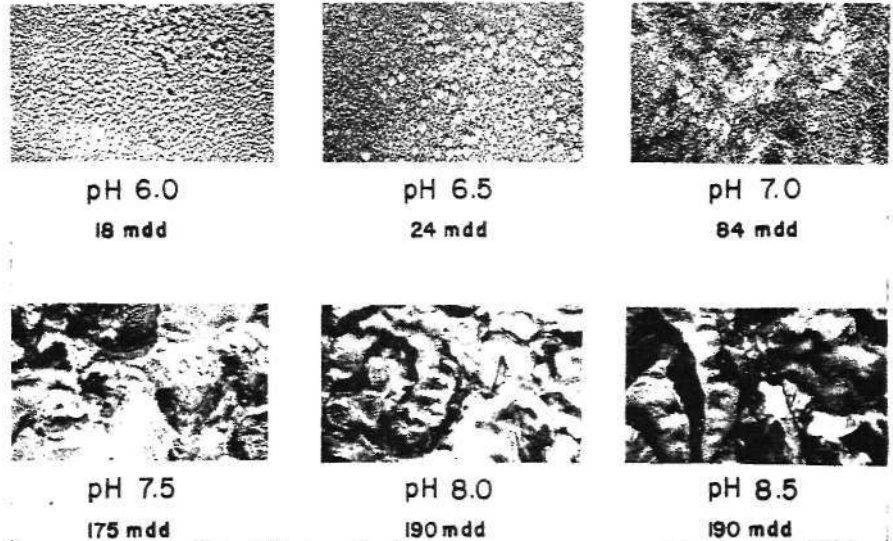


Figure 5—Corrosion products on steel specimens used to obtain data given in Figure 4. Samples shown are actual size.

Also, the inside surface is found to be highly resistant to corrosion by water, but when this surface is machined or ground, the resistance disappears. In the absence of calcium or large concentrations of corrosion inhibitors, each quality of water tested was found to cause corrosion of ground-surface cast iron.

Grinding of Cast Iron Pipe Interiors

It was learned, from personal plant inspection and correspondence, that the interior of all centrifugally cast pipe is partially ground for the purpose of reducing roughness prior to the application of coal tar coating or cement lining. In this process, most cast iron pipe interiors are ground to the extent of 10 to 50 percent of the surface.

Because most cast iron pipe in service is tar coated, it appears that tuberculation in such pipe results from slight but significant corrosive action of partially inhibited water on holidays, or minute holes, that occur in the tar coating covering the machined areas.

To determine the composition on the interior "skin" of the non-ground pipe surface responsible for the remarkable corrosion resistance, a specimen was submitted to Professor W. H. Bruckner of the University of Illinois Department of Metallurgy. Figure 6 shows a microphotograph of an unetched mount.

When the "skin" on the internal surface of the pipe was scraped, the black phase between the metal surface and the gray phase was found to be ferromagnetic (Fe_3O_4) with a cubic structure.

The gray phase on the exposed surface, adjacent primarily to the magnetite, showed two or more components under polarized light: long needle-like pyroxenes of monoclinic structure as CaSiO_3 or FeSiO_3 (Mg or Mn); and polyhedron garnet of cubic structure, such as $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_2$ or $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_2$.

It appears that this silicate "skin", which is highly insoluble, may provide an effective barrier to corrosion by water. It is very brittle and therefore is not a completely effective barrier.

Further studies⁶ were devoted to ground-surface specimens of cast iron in waters containing calcium.

Concentration of Calcium

A broad generalization of these data indicates (Figure 7) that the concentra-

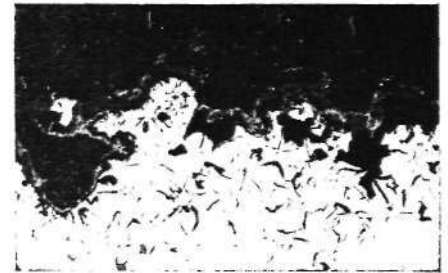


Figure 6—Microphotograph of an unetched mount of cast iron pipe showing the non-ground pipe surface. Original magnification, 100X; actual magnification after reduction for engraving purposes, 26X.

tion of calcium in the presence of alkalinity is a primary factor in the inhibition of corrosion of machined cast iron. This generalization appears to be evident irrespective of the saturation index for CaCO_3 solubility, of velocities from 0.085 to 0.85 fps, of minor variations in chloride/alkalinity ratio, or of the presence or absence of chlorine, chloramine, or silica. It also appears that the specimens must be exposed a certain length of time at these velocities before the inhibition occurs.

In this generalization, representing all tests, there are broad variations in rates of corrosion (as much as tenfold for each level of calcium.) These variations will be indicated for specific modifications in water quality, first at the 125 ppm calcium hardness level. The data are represented as smooth lines from the average rates, determined five times per week for triplicate specimens.

Figure 8 shows the reduction in corrosion rates with time for three degrees of saturation with respect to calcium carbonate at a low velocity of 0.085 fps. The decrease in rate of corrosion occurred most rapidly in water at -0.1 saturation index and least rapidly at -0.8 saturation index.

The specimens in water at -0.3 saturation index leveled off at a higher final corrosion rate than either of the other two previously mentioned. It should be indicated that the specimens at this saturation index showed small dark reddish spots or growths surrounded by an over-all whitish red deposit, even prior to the addition of chlorine, and these spots continued to form tubercles. Simi-

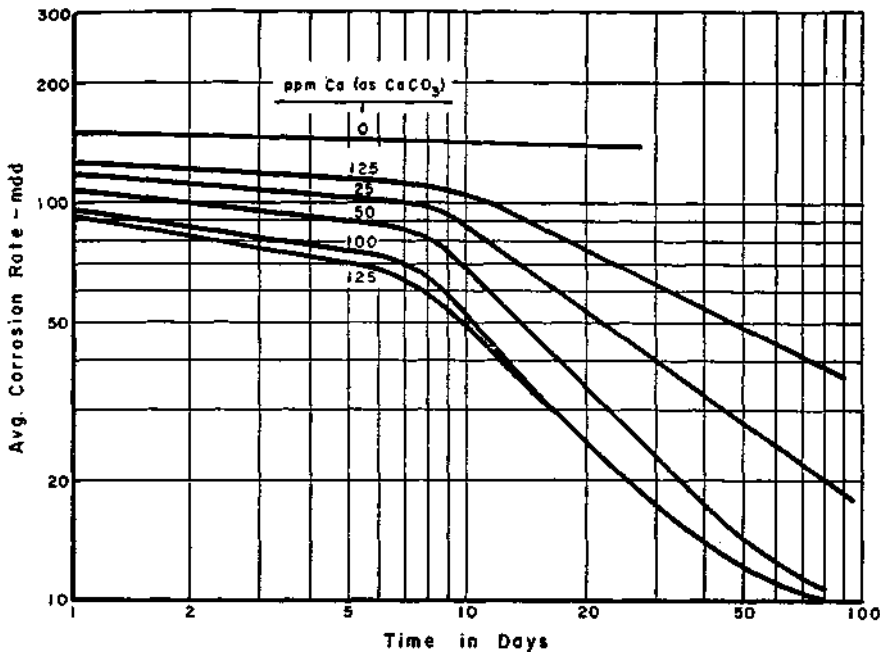


Figure 7—Generalized summary of data showing the effect of calcium, with alkalinity, on the corrosion of machined cast iron. Alkalinity was 125 ppm (as CaCO₃) and velocity range was 0.08 — 0.85 fps. Tests were made at room temperature.

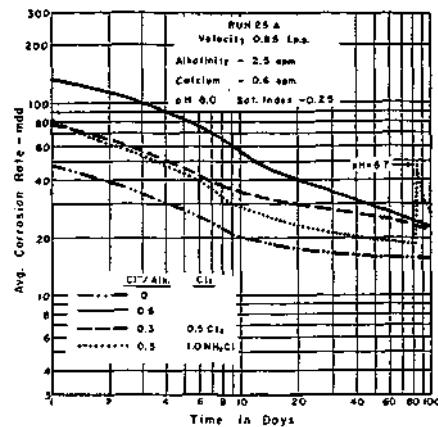


Figure 10—Corrosion rate variation with time for machined cast iron at 0.85 fps.

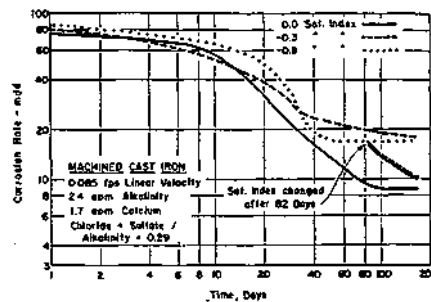


Figure 11—Corrosion rate variation with time for machined cast iron at 0.085 fps.

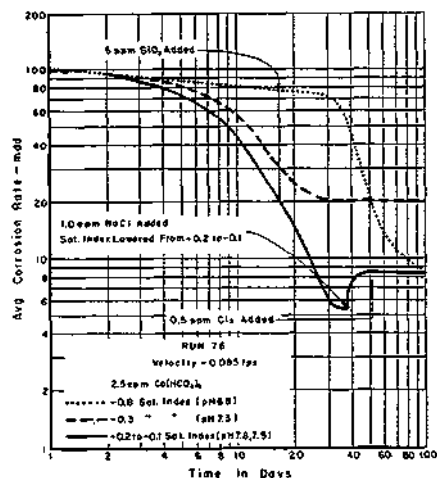


Figure 8—Corrosion rate variation with time for machined cast iron at 0.085 fps.

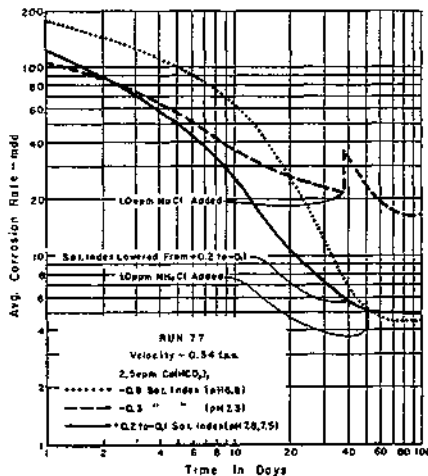


Figure 9—Corrosion rate variation with time for machined cast iron at 0.34 fps.

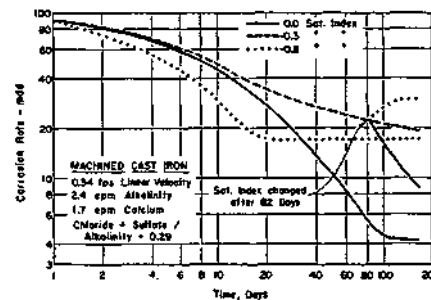


Figure 12—Corrosion rate variation with time for machined cast iron at 0.34 fps.

lar growths, but to a lesser extent, developed on the specimens in water at -0.1 saturation index.

The effect of adding 56 ppm sodium chloride increased the corrosion rate. A later illustration shows that the simultaneous reduction of saturation index was not responsible for the increase in rate at this high calcium level.

The single addition of 5 ppm SiO₂ after 17 days had no apparent effect on the corrosion rate. No attempt was made in this test to maintain this concentration.

Figure 9 provides similar data at 0.34 fps, but with chloramine present rather than free chlorine. The more rapid reduction of corrosion rate and the lower final corrosion rates testify to the effectiveness of greater velocity to improve the diffusion rate of calcium as the inhibitor. Reducing the saturation index had no effect on the corrosion rate with this relatively high calcium content.

Tubercles, similar to those occurring when free chlorine was present, were noted in the -0.3 saturation environ-

ment, but they were smaller in size and number.

The effect of adding 56 ppm sodium chloride after 36 days is clearly demonstrated.

Relative Influences

The relative influences of calcium concentration, saturation index, the chloride to alkalinity ratio, and chlorine were further investigated. The results of four test conditions using waters of 30 ppm calcium hardness are indicated in Figure 10. These specimens showed tuberculation in all cases, with or without chlorine or chloramine, and were similar in appearance to the specimens in water of 125 ppm calcium hardness at -0.3 saturation index, in Figures 8 and 9.

Although the calcium concentration was lower, the rate of corrosion after one day was less than that when 125 ppm calcium hardness was present since the velocity was greater and the pH higher. The rate of approach to equilib-

rium is slower than when 125 ppm calcium hardness was present.

Recent data provide results for water with 85 ppm calcium hardness and a 0.29 (Cl+SO₄)/alkalinity ratio. Various proportions of chloride and sulfate were used, but in these tests, no different rates of corrosion or degree of tuberculation were noted with sulfate than with chloride. The data have been grouped by velocities: 0.085 fps, 0.34 fps, and 0.85 fps. The results show the same general trend as exhibited in the data shown in Figures 8 and 9.

At the low velocity (Figure 11), the specimens in the water at zero saturation index had a faster rate of decrease and ended at a lower final rate of corrosion than those in waters of either the -0.3 or -0.8 saturation index. After 82 days, the saturation index was made more positive in two of the four solutions at -0.8 saturation index. There was an immediate decrease in corrosion rate for the change to both zero and -0.3 saturation index with this water of low calcium concentration.

At the intermediate velocity (Figure 12), the specimens generally had a

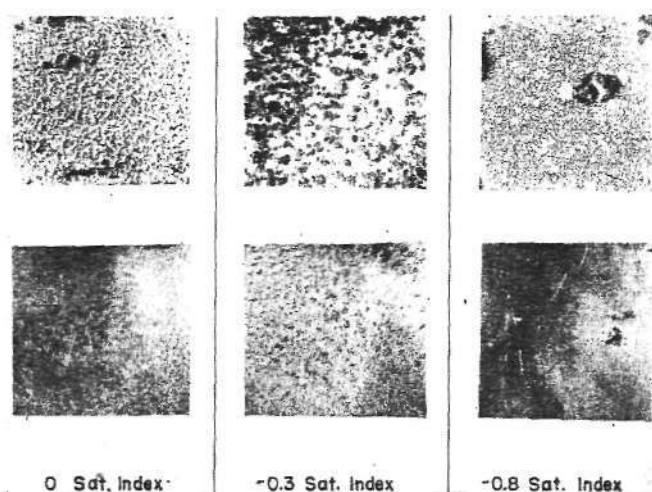


Figure 13—Typical corroded surfaces of cast iron specimens used to obtain data in Figure 12. Specimens are shown before and after cleaning.

slightly greater decrease of corrosion rate than at the low velocity. For an undetermined reason, the specimens in water at -0.8 saturation index reached their equilibrium rate much quicker than did the specimens in waters at either the zero or -0.3 saturation index. The zero saturation index, however, provided the lowest final rate of corrosion. A change in saturation index after 82 days from -0.3 to -0.8 resulted in an increase of the corrosion rate, whereas a change in the positive direction to zero saturation index resulted in a decrease of the corrosion rate.

Typical specimens for the three degrees of saturation index with respect to calcium carbonate are shown before and after cleaning in Figure 13.

Specimens at the high velocity (Figure 14) had lower initial corrosion rates. However they had a slower rate of approach to equilibrium, similar to the results shown previously in Figure 10. A change from zero to -0.8 saturation index after 82 days resulted in an increase in the corrosion rate. The change from zero to -0.3 saturation index apparently was not significant enough to change the corrosion rates.

The specimens in water at -0.8 saturation index showed primarily a general corrosion attack as did the specimens in tests at the other velocities and at 125 ppm calcium hardness.

The specimens in water at -0.3 saturation index had a rough surface of corrosion products. Tubercles occurred over the entire surface of the specimen.

The specimens at zero saturation index exhibited corrosion products similar to those occurring in water at -0.3 saturation index; however, there were fewer and less pronounced tubercles.

Discussion.

1. It has been established that bicarbonate in the absence of calcium is a mild, although effective inhibitor to corrosion of steel, as contrasted to the accelerative effect of chloride and sulfate anions. Alkalinity, a measure of bicarbonates, exerts a singular or independent inhibiting effect on corrosion.

2. It also has been established that calcium hardness, independent of the saturation index, is a mild, although effective inhibitor to corrosion. It is probable that this is the case only in the presence of alkalinity.

3. The finding that calcium in the presence of alkalinity, regardless of pH

or saturation index, is an effective inhibitor to corrosion is not inconsistent with theory and experience. This is because the basic corrosion reaction is conducive to the formation of calcium carbonate at the cathode points in the corrosion cell even though the water environment is below saturation with respect to calcium carbonate. The rate at which such deposition may take place is increased by higher concentrations of calcium and/or presumably the alkalinity. The rate of deposition also is increased by higher velocities. The rate is further increased by pH adjustment at or above the saturation pH for calcium carbonate.

4. The finding that tubercles form under conditions below, but near, complete protection is consistent with the well-known action of inhibitors to induce pitting corrosion, rather than general corrosion, when present in a concentration that is insufficient to produce complete protection. This relation is confirmed by the observation of pitting corrosion or "deferritization" on the specimens which showed tuberculation. The fact that tubercles do form apparently is due to the deposition of a supporting structure of calcium carbonate with or in the normal corrosion product of ferric hydroxide in aerated waters.

If the saturation index is not sufficiently close to zero or the concentrations of calcium and/or alkalinity are too low, a supporting structure may not be developed, although appreciable protection may be afforded by calcium carbonate imbedded in the rust deposit from generalized corrosion. It was observed on specimens in waters of -0.8 saturation index with high calcium at pH 6.8 (Figures 8 and 9) that the specimens were coated with a whitish red deposit of sufficient thickness (about 1/16 inch) and rigidity to continue to adhere even though this deposit was cracked for distances of one-half inch. There were no pits under this deposit and it served as an effective barrier to the diffusion of oxygen and other corrosive agents.

Conclusions

1. As deduced from the data derived from these tests, the corrosivity of air-saturated domestic waters is dependent on: (a) the proportion of corrosive agents to the inhibitive agents, (b) the concentration and degree of effectiveness of the corrosive and inhibitive agents and (c) the velocity of flow which influences

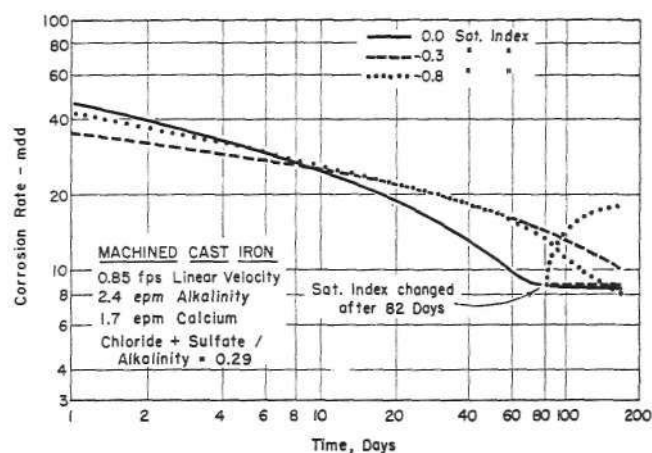


Figure 14—Corrosion rate variation with time for machined cast iron at 0.85 fps.

the rates of diffusion of both the corrosive and inhibitive agents to or through the protective surface.

Corrosive agents in domestic waters are chloride and sulfate ions. Inhibitive agents in domestic waters are bicarbonate, carbonate, hydroxide, and calcium ions. The relative effectiveness of each is not definitive and may be influenced by one or more of the others.

It is axiomatic that for each specific condition, a minimum concentration of the inhibitor must be present for complete protection.

Increasing velocity provides increasing protection with low proportions of corrosive agents to inhibitive agents. On the other hand, with increasing velocities, as this proportion increases, the degree of protection decreases.

2. The intermediate proportions of corrosive to inhibitive agents, which result in incomplete protection at a particular velocity, are conducive to pitting and/or tuberculation. The problem of designing water treatment to avoid tuberculation of cast iron is limited to such waters as already contain inhibitors, but which are in concentrations which are insufficient to provide complete protection. The problem is jointly concerned with maintaining or creating a velocity of flow which is sufficient to provide adequate diffusion, transport, or movement of the inhibitor to the point of effectiveness.

Acknowledgment

These studies are supported by Research Grant G-4007 (R) from the National Institutes of Health, U. S. Public Health Service. The physical facilities for the laboratory investigations were furnished by the Illinois State Water Survey. The authors wish to thank Mary C. Brooks and Wesley Walters of the Illinois State Water Survey for their laboratory assistance.

References

1. T. E. Larson. Report on Loss in Carrying Capacity of Water Mains. *Jour. AWWA*, 47, 1061-72. (1955) Nov.
2. R. V. Skold and T. E. Larson. Measurement of the Instantaneous Corrosion Rate by Means of Polarization Data. *Corrosion*, 13, 139-42. (1957) Feb.
3. M. Stern. A Method for Determining Corrosion Rates from Linear Polarization Data. Submitted to *Corrosion* for publication.
4. O. B. J. Fraser, D. E. Ackermann and J. M. Sands. Controllable Variables in the Quantitative Study of Submerged Corrosion of Metal. *Ind. Eng. Chem.*, 19, 332 (1927).
5. G. E. Whitman, R. P. Russell and V. J. Altieri. Effect of Hydrogen Ion Concentration on Submerged Corrosion of Steel. *Ind. Eng. Chem.*, 16, 665 (1924).
6. T. E. Larson and R. V. Skold. Corrosion and Tuberculation of Cast Iron. *Jour. AWWA*, 49, 1294-1302 (1957) Oct.