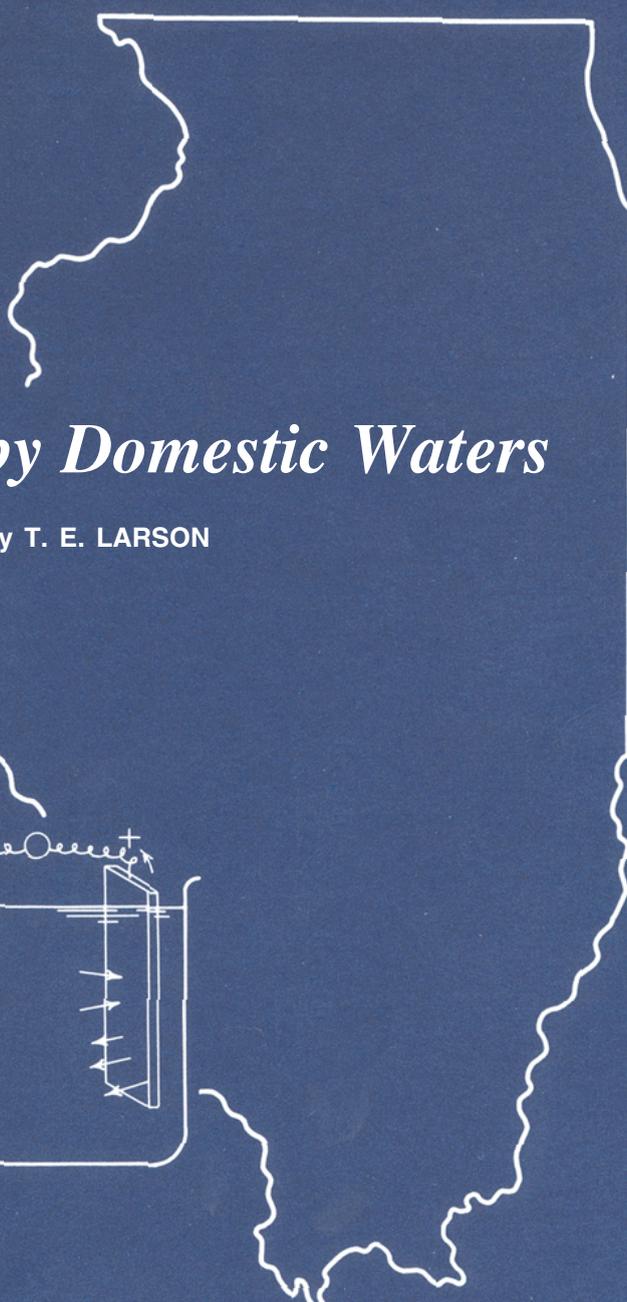


ISWS-75-BUL59
BULLETIN 59
STATE OF ILLINOIS
DEPARTMENT OF REGISTRATION AND EDUCATION



Corrosion by Domestic Waters

by T. E. LARSON



ILLINOIS STATE WATER SURVEY

URBANA
1975

BULLETIN 59



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by T. E. LARSON

Title: Corrosion by Domestic Waters.

Abstract: Essential data on corrosion gathered by the Illinois State Water Survey in isolated or programmed studies, and from experience at state institutions since 1950, are summarized. A brief review of basic fundamentals of corrosion is presented as background for the summaries. Also included are some of the general and specific recommendations concerning inhibitors and construction materials that were developed through laboratory and field evaluations for use by architects, engineers, and institutional maintenance personnel. Appendixes contain a discussion of corrosion in water wells and pumps and two ancillary papers for orientation and recognition of other factors related to distribution system water quality.

Reference: Larson, T. E. Corrosion by Domestic Waters. Illinois State Water Survey, Urbana, Bulletin 59, 1975.

Indexing Terms: Construction materials, corrosion, corrosion control, distribution systems, laboratory tests, metals, water chemistry, water quality.

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**URBANA
1975**

Printed by authority of the State of Illinois—Ch. 127, IRS, Par. 58.29

(6-75-1500)



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INTRODUCTION

It is the purpose of this publication to summarize the essential data on corrosion by domestic waters gathered by the Illinois State Water Survey in isolated studies and programmed research, as well as knowledge gained from experience at state institutions since 1950. Domestic water is here defined as any water provided for human consumption and allied uses, in contrast to sea water, brines, or conventional sewage effluents.

In 1939, a questionnaire was mailed to 470 Illinois water supply plants that had been in existence for over 5 years to assess the magnitude of corrosion problems. Replies from 191 superintendents showed that 41 percent of these water supply systems had corrosion problems involving water mains, service lines, elevated tanks, and well pumps.

Beginning in 1943, field studies on deep well turbine pumps that had been removed for repair were made over a period of 6 years and resulted in 6 publications. A summary of the fundamental findings is included as appendix A. With the subsequent development of reliable submersible pumps, those problems are now of minor importance.

In 1948, a study of corrosion of steel at low flow velocities laid the groundwork for subsequent studies.

In 1949, the Water Survey was requested to prepare specifications for chemicals used in some of the state institutions and to supervise the application of these chemicals. The purpose for the specifications was to permit realistic competitive bidding, which was formerly impossible with proprietary formulations. This led to the uncovering of costly problems of corrosion and maintenance at the institutions, i.e., scale and corrosion in both low and high pressure boilers, condensate lines, cooling towers, distribution systems, hot water systems, and a host of ancillary problems with swimming pools, faucets, valves, and laundry facilities.

Since that time, corrective measures have been taken and means for assessment of their effectiveness have been developed. Laboratory and field evaluations of inhibitors and construction materials have provided a breadth of experience and knowledge which has permitted the development of general and specific recommendations to architects, engineers, and maintenance personnel at the institutions. Where possible, those recommendations related to distribution systems have been included in this text.

In 1953, the American Water Works Association re-

quested the Water Survey to conduct a study on loss in carrying capacity in distribution systems. This was supported in part by grants RG 4007 and WP 132 from the National Institutes of Health, U. S. Public Health Service, from May 1, 1954, to September 30, 1968, resulting directly in seven publications and indirectly in five others. Summaries of the fundamental findings related to corrosion of cast iron are included, generally in sequence with time, as a part of this publication. In all, about 30 years of corrosion studies contribute to this summary of findings. Since 1968 other studies have been made as time and financial support has been available.

Beyond the laboratory and field research summarized in this report is the obvious need for summaries of basic fundamentals of corrosion that have been accumulated over some 50 to 60 years. It is readily conceded that a great number of authors have contributed to this literature. This publication does not pretend to include a complete review of the literature, and only a few key references are used in the text on principles. These are felt to be necessary to present additional background for the summaries of the studies and to round out the presentation.

Finally, two other ancillary papers are included as appendixes for orientation and recognition of other factors related to distribution system water quality. Appendix B describes the dynamic nature of distribution systems and the problems that can exist. Appendix C documents actual changes in water quality resulting from microbiological growths to the point of removal of all oxygen, and then further changes under anaerobic conditions in a 6500-foot isolated water line at the end of the system.

Acknowledgments

Grateful acknowledgment is made for the administrative support for these studies by Dr. A. M. Buswell and Dr. William C. Ackermann, former Chief and current Chief of the Water Survey, respectively. Co-participants from the Water Survey (in chronological order) who contributed much to the findings presented herein are: John Grench, Wesley Walters, Mary C. Brooks, Donna Winn, R. M. King, R. V. Skold, E. Savinelli, Donal E. Etter, L. M. Henley, R. W. Lane, F. W. Sollo, Jr., H. W. Humphreys, and J. C. Neill.

Cast iron specimens were provided by the U. S. Pipe and

Foundry Company and special apparatus was contributed by the American Cast Iron Pipe Company. Steel specimens were provided by the U. S. Steel Company. Advice and support was provided by the AWWA Advisory Committee, consisting of E. S. Cole, E. E. Erickson, Ed Farmer, J. A.

Frank, A. E. Griffin, Leo Louis, W. E. MacDonald, S. T. Powell, M. J. Taras, and E. F. Wagner.

Mrs. Patricia A. Motherway edited the report, Mrs. Suzi O'Connor typed the final manuscript, and John Brother, Jr., and William Motherway, Jr., prepared the illustrations.

FUNDAMENTALS OF CORROSION

Corrosion may be defined as the destruction of a metal usually by chemical or electrochemical reaction with its environment.¹ Whether it be in the atmosphere, immersed in water, or buried in the ground, a metal may be subject to chemical interaction with environmental elements.

Most metals are derived from natural mineral ores, and when exposed to the elements of the environment, they have an inherent tendency to revert to the stable forms in which they were originally found in the earth. A common example of this tendency is the rapid formation of iron rust when an unprotected common steel surface is in contact with water or humid air. Rust may be in the form of any of the native oxide forms in iron ore.

Different metals and alloys have greater or lesser *tendencies* to corrode, or to revert to their natural forms. This tendency is expressed by the relative electrochemical potential related to a hydrogen electrode or to other standardized electrodes in a given water environment. The potential is

a measure of the oxidation and reducing characteristics of the interface between the metal and the water, and the relative electrochemical potentials of two different metals determine which metal has the greater tendency to corrode.

However, the *rate* of corrosion is dependent largely on the inhibition or resistance to continuing progress of the reaction by the products of corrosion in the particular water environment. This inhibition, which controls the rate, is dependent on the metal itself and a variety of conditions involving the ionic components in the water as well as dissolved oxygen, carbon dioxide, temperature, and configuration of the structure and movement of the water.

A generalized galvanic series of metals and alloys¹ has been developed and is shown in table 1. It has not been practical to tabulate voltage values, because these will vary with the water environment, but in general the grouped metals have similar potentials. This galvanic series indicates that the least noble metals have the greatest tendency to corrode, and the most noble metals have the least tendency to corrode. When metals from different groups are coupled and exposed to the water environment, the more noble metal is cathodic to the less noble metal which then corrodes and protects the more noble metal. This is called galvanic action. The farther apart the metals stand in the series the greater the galvanic tendency. The rate of corrosion increases with an increasing relative surface area of the cathodic metal to the anodic area.

Table 1. Galvanic Series of Metals and Alloys

<i>Corroded end (anodic, or least noble)</i>	Inconel (active)
Magnesium	Hastelloy A
Magnesium alloys	Hastelloy B
Zinc	Brasses
Aluminum 2S	Copper
Cadmium	Bronzes
Aluminum 17ST	Copper-nickel alloys
Steel or iron	Titanium
Cast iron	Monel
Chromium-iron (active)	Silver solder
Ni-Resist*	Nickel (passive)
18-8 Cr-Ni-Fe (active)	Inconel (passive)
18-8-3 Cr-Ni-Mo-Fe (active)	Chromium-iron (passive)
Hastelloy C	18-8 Cr-Ni-Fe (passive)
Lead-tin solders	18-8-3 Cr-Ni-Mo-Fe (passive)
Lead	Silver
Tin	Graphite
Nickel (active)	Gold
	<i>Protected end (cathodic, or most noble)</i>

* Registered U. S. Patent Office

Types of Corrosion

Each type of corrosion has its own characteristics and offers clues to the causes and sometimes to the characteristics of the environment. Possible types of control may also be deduced from the clues.

Uniform corrosion is recognized as taking place at a generally equal rate over the surface. The loss in weight is directly proportional to the time of exposure and the rate of corrosion is constant. This type of corrosion is usually associated with acids or with water having a very low pH and very few protective properties. Mild steel in neutral, low-calcium, and low-alkalinity salt water corrodes at a rather uniform rate.

When the corrosion rate is uniform it is possible to deter-

mine the weight loss over a time interval and relate this to the electrochemical equivalent as follows:

$$\text{Weight loss/time} = k i$$

where k is the electrochemical equivalent and i is the total corrosion current. Although the corrosion current cannot be measured, it may be estimated from the equation when the weight loss per time is known.

Pitting corrosion is nonuniform and more generally observed than uniform corrosion. It occurs in an environment which offers some but not complete protection. The pit develops at a localized anodic point on the surface and continues by virtue of a large cathodic area surrounding the anode. Chloride ions are particularly notorious for their association with this type of corrosion of steel. Even stainless steel is subject to pitting corrosion with relatively high chloride solutions. Pits may be sharp and deep or shallow and broad, and can occur without chlorides. In water containing dissolved oxygen, the oxide corrosion products deposit over the site of the pitting action and form tubercles.

Pitting corrosion may also be associated with galvanic corrosion, concentration-cell corrosion, and crevice corrosion, particularly during low flow or stagnant conditions.

Galvanic corrosion is associated with the contact of two different metals or alloys in the same environment. Almost all metals and substances have different solution potentials, whether in the same or in different environments. When two metals come together, the difference in potential results in current flow, and one of the metals becomes anodic to the other, which serves as the cathode (see table 1). The anodic metal corrodes and the cathodic metal does not (or if so at a relatively low rate). *The cathodic metal is said to be protected at the expense of the anodic metal.* To be exact, all corrosion is galvanic in the sense that an electrochemical cell is the source of the corrosion current.

The rate of galvanic corrosion is increased by greater differences in potential between the two metals. It is increased by large areas of cathode relative to the area of the anode. It is generally increased by closeness of the two metals and also by increased mineralization or conductivity of the water.

Galvanic corrosion is often a great source of difficulty where brass, bronze, or copper is in direct contact with aluminum, galvanized iron, or iron. Copper-bearing metals are cathodic to aluminum, zinc, and iron, and their under-water contact very often results in corrosion of the latter metals. Similarly, mill scale on steel is cathodic to the steel; iron oxide is cathodic to iron; cement is cathodic to copper; carbon is cathodic to iron; iron is cathodic to aluminum and to zinc.

Galvanized (zinc-coated) steel is usually more serviceable than steel alone, because the iron exposed at joints and holidays is protected at the expense of the zinc. In general, longer life may be expected with greater thickness of the

zinc coating. Zinc in many natural waters containing alkalinity of 50 to 100 mg/l or more will form an insoluble protective coating of basic zinc carbonate in the pH range of 7.5 to 8.5 at room temperature or lower. In hot-water tanks, there is some evidence that zinc becomes cathodic to iron at temperatures above 140 to 160°F with certain types of waters. Traces of copper (0.1 mg/l) in the water can 'plate out' on zinc or iron and result in local pitting. Waters containing copper have a similar, more serious, effect on aluminum.

Concentration-cell corrosion is perhaps the most prevalent type of corrosion, and because it is difficult to ascertain by field measurement, it is usually deduced by inference. This type of corrosion occurs when there are differences in the total or the type of mineralization of the environment. Differences in acidity (pH), metal-ion concentration, anion concentration, or dissolved oxygen cause differences in the solution potential of the same metal. Differences in temperature can also induce differences in the solution potential of the same metal.

It has been noted (page 6) that in water containing dissolved oxygen, the corrosion products deposit at the anode, and in the secondary reaction of oxidation of ferrous iron to ferric iron and subsequent hydrolysis, hydrogen ions are formed. This greater acidity at the anode results in a hydrogen-ion concentration cell at this point, and increases the rate of corrosion. In the same instance, dissolved oxygen cannot diffuse or penetrate to the anode surface because it first reacts with the ferrous iron; thus, there is an absence of oxygen at the anode. But oxygen can diffuse to the cathode area and result in an oxygen concentration cell which also increases the rate of corrosion at the point of absence of oxygen. Hydroxide ions accumulate at the cathode area, resulting in drastic reduction in hydrogen-ion concentration, which therefore enhances the concentration cell related to the development of hydrogen ions at the anode.

It should be noted that although the dissolved oxygen usually stimulates corrosion, the loss in metal takes place at the anode, where there is no dissolved oxygen.

Oxygen concentration cells develop at water surfaces exposed to air, accelerating corrosion a short distance below the surface. The dissolved oxygen concentration is replaced by diffusion from air and remains high at and near the surface, but does not replenish as rapidly at lower depths because of the distance for diffusion. Therefore, the corrosion takes place at a level slightly *below* the surface rather than at the surface.

Dirt and debris or local chemical precipitates on a metal surface hinder oxygen diffusion by covering the metal at local areas. Thus, corrosion takes place under the deposit.

Thus it is evident that any nonadherent deposition on metal can start a chain of circumstances which result in an oxygen concentration cell.

Crevice corrosion might be classed as a form of concentration-cell corrosion because when oxygen is spent on corrosion in a crevice, it is difficult for more oxygen to reach the metal by diffusion into the depths of the crevice. The crack, crevice, or uneven joint between two surfaces of the same metal bound together face to face behaves as a pit where oxygen can reach the exposed surface but becomes deficient in the crevice, thus forming an oxygen concentration cell where corrosion takes place.

Dezincification is the result of removal of zinc from its alloy with copper (brass). Copper remains at the surface of the brass as the zinc is dissolved. Soft unstable waters, especially those with a high CO₂ content, are particularly aggressive to Muntz metal and yellow brass. Red brass and Admiralty metal are more resistant. The occurrence of plug-type dezincification and dezincification at threaded joints suggests that debris and crevices may initiate oxygen concentration cells and result in dezincification.

Graphitization is a form of corrosion of cast iron in highly mineralized water or waters with a low pH, which results in the removal of the iron silicon metal alloy making up one of the phases of the cast iron microstructure. A black, spongy-appearing, but hard mass of graphite remains. The graphite dispersed in the cast iron serves as the cathode for a large number of small galvanic cells, and the iron-silicon alloy becomes the anode.

Cast-iron products derive their shape from the freezing of a liquid alloy in a mold; thus solidification takes place under different conditions over the cross section of any cast shape. The portion near the mold wall may have a different composition, freezing rate, and structure than the material farther from the mold wall. There is likely to be less graphite at the surface of the casting; thus we have the familiar observation that machining of cast iron produces a lower corrosion resistance at the machined areas.

The high corrosion resistance of cast iron in soil is probably due to the formation of a silicate film at the surface which together with the initial corrosion products forms an effective barrier. In mine water having a low pH and high concentration of iron and/or copper salts, the silicate film may be quite soluble. The removal of the film then causes rapid corrosion of the metallic phases of the cast iron, leaving the skeleton of graphite embedded in corrosion products.

Stress corrosion results from tensile stress, usually of external origin, on the metal or alloy. The corrosion usually (but not always) takes place selectively at the microstructure grain boundaries in the metal. Repeated rupture of a protective film on the surface provides a continuously anodic region.

Corrosion fatigue resulting from alternate stress conditions is usually more rapid than steady-state stress corrosion. The alternation of the stress disturbs such protective

film as may develop at the anode site and enhances the rate of corrosion.

Erosion corrosion results from the removal of the protective film of corrosion products which serves as a barrier to corrosive attack of some metals. Many metals such as aluminum, austenitic stainless steel, and passive iron are completely protected by a film (such as aluminum oxide on aluminum in favorable environments). The erosion, generally at high velocity, may take place through removal of the film by abrasive, suspended material. Friction between two adjoining surfaces may also permit corrosion to continue.

Impingement attack on copper pipe is also an example of apparent erosion corrosion, as it is particularly evident at velocities greater than 5 to 8 feet per second (fps) and at sudden changes in direction of flow at joints and elbows.

Cavitation corrosion is usually associated with high velocity and sudden changes in velocity direction which causes gas-bubble formation at low pressure points and resolution of the gases at high pressure points. The attack occurs downstream from the direction change caused by a constriction such as a valve or protrusion at a joint. Carbon dioxide in the gas bubbles develops an acidic film at the water surface. If oxygen is present, its concentration at the water surface is also greater than in the body of the water and further accelerates corrosion.

Wire drawing in faucet seats appears as grooves across the face of the seat. Apparently this is a type of cavitation corrosion or erosion corrosion in which chloramine serves as a corrosion accelerator. Monel metal seems to be the only alloy that resists this type of attack.

Stray currents have often been blamed for corrosion occurrences where other causes have been present. With direct-current electric railways, serious corrosion problems with underground structures have properly been traced to stray currents, but almost invariably this has been external corrosion of piping rather than internal. All metals have greater conductivity than the surrounding environment, and current will stay with the metal until there is a discontinuity. An excess of electrons will leave the metal at the points where the environment is more highly conductive and closest to another conductive receptor for the current. Corrosion takes place at the anode, the point where the current leaves the metal to be returned to the power source. Currents seek out and travel by the path of least resistance.

The use of insulating connections or proper counter-current applications such as cathodic protection can eliminate this problem. However, improper use without a satisfactory survey of the problem and advice by specialists, can result in accelerated corrosion rather than prevention.

Principles

Although destruction of metals can result from direct chemical reactions, it is more generally considered as an

electrochemical process. In the water environment, this process is usually destructive to materials of construction, but it may also present conditions conducive to protective reactions.

It is generally accepted that corrosion results from the flow of electric current between electrodes or anodic and cathodic areas on the metal surface. These areas may be microscopic and in very close proximity, thereby causing generally uniform corrosion and often 'red' water; or they may be large and somewhat remote from one another and cause pitting, with or without tuberculation. Potential differences may be induced by various conditions, some by the characteristics of the metal and some by the character of the water at the boundary surface or interface. Especially significant are variations in the composition of the metal or the water from point to point on the contact surface. Impurities in the metal, sediment accumulations, adherent bacterial slimes, accumulations of the products of corrosion – all are related either directly or indirectly to the development of anodic and cathodic areas for corrosion circuits.

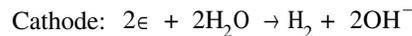
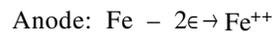
In almost all forms of pipe corrosion, the metal goes into solution at the anode areas. Because electrons are released to the surface when the metal dissolves, the metal develops an electrical potential. Electrons liberated at these areas flow through the metal to the cathode areas where they become involved in another chemical reaction and the metal develops another electrical potential. Control of corrosion by water treatment methods aims at retarding either or both of the primary electrode reactions.

Because electric currents are carried by ions, as conductors in water, and because these ions affect the potentials at both the anode and cathode, some discussion of the soluble components in water is warranted.

To some extent, almost all mineral salts dissolve in water, from insignificant traces to gross concentrations exceeding that of salt in sea water. On solution, these salts separate into two types of ions, anions and cations. These ions have opposite electric charges and are kept apart by the water itself. These ions are responsible for the ability of water to conduct an electric current. Pure water has relatively few ions. Only one one-hundred thousandth of one percent of water separates into hydrogen cations and hydroxyl anions. Therefore, pure water, free from mineral salts, has very little capacity for carrying electric current. Its electric conductivity therefore is extremely low.

However, when minerals are dissolved in water, the resultant ions provide the necessary conductivity to permit the corrosion current to flow, with negatively charged anions moving to the anode and positively charged cations moving to the cathode. Their accumulation at the respective electrodes is limited by other reactions which take place at these points.

The basic electrode reactions involving the transfer of electrons may be represented as follows:



When dissolved oxygen is present, the cathode reaction may be represented as: $2\epsilon + \text{H}_2\text{O} + 1/2 \text{O}_2 \rightarrow 2\text{OH}^-$. Therefore, with or without dissolved oxygen, the same amount of hydroxide ion is formed at the cathode and an alkaline condition prevails.

Effect of Dissolved Oxygen

The most prevalent and at the same time the most potent of the common corrosive agents is dissolved oxygen. Oxygen in any form of water, be it humidity, rain, drinking water, or sea water, has long been recognized as a destroyer of ferrous metals. When present in public water supplies its concentration may range from a few mg/l to as much as 14 mg/l. This is usually small in comparison with other ingredients. It is no more than half the concentration of nitrogen, for example.

As the water passes through a distribution system, rarely is more than 1 mg/l of oxygen used up in corroding the metal, except in low-circulation areas or dead ends. At a 5-fps velocity in a 24-inch main, it is doubtful that a change in dissolved oxygen of more than 0.1 mg/l per mile ever occurs. But this is a continuous supply, a continuing feed of this destroyer to the pipe wall over years of service.

Were water of this same oxygen concentration used in a home hot-water heating system largely composed of steel with no replenishment or replacement of the water, the system would last indefinitely, because the limited supply of oxygen would be quickly removed, and little or no corrosion would then be possible.

The discovery of a method more economical than mechanical deaeration for removing dissolved oxygen from water could reduce the present serious corrosion by at least 90 percent. Many years ago Speller² showed that passage of water through iron filings removed dissolved oxygen, but this technique is hampered by the problem of replenishment of the filings and clogging of the filters.

Minerals and the Electrolytic Cell

If sodium chloride was the only mineral present, the negative chloride anions would be attracted to the positive anode where Fe^{++} is present, and the positive sodium cations would be attracted to the negative cathode (see figure 1a). Thus at the cathode there would be a sodium hydroxide solution, and at the anode a soluble ferrous chloride solution. But, with dissolved oxygen present, the ferrous chloride solution is oxidized to form ferric chloride, part

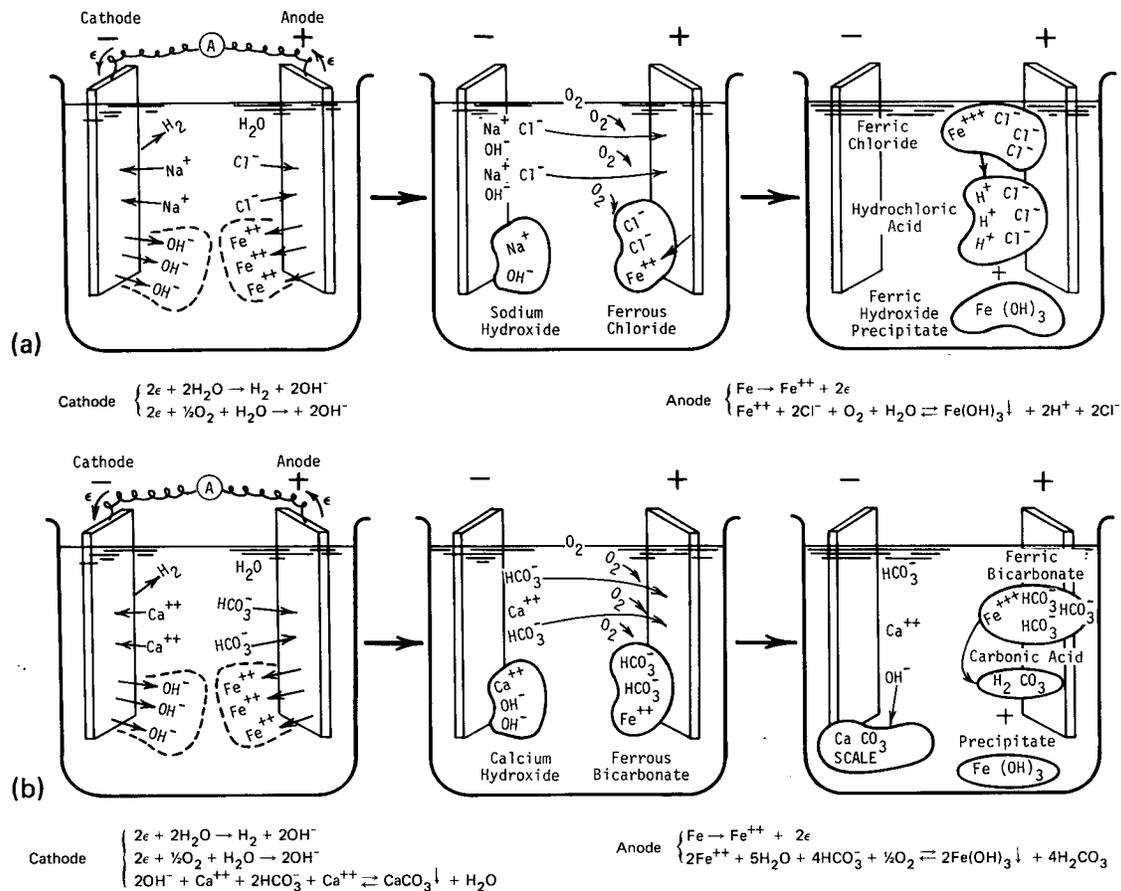


Figure 1. Electrolytic corrosion of iron in a) sodium chloride solution and b) calcium bicarbonate solution

of which in turn reacts with water itself to form an insoluble ferric hydroxide and hydrochloric acid



Therefore, at the anode there is a mixture of dilute hydrochloric acid with a solution of ferrous chloride and a precipitate of ferric hydroxide. This is then the major corrosion product.

The high pH at the cathode in the presence of dissolved oxygen and low pH at the anode increases the potential difference between the electrodes, and thus increases the corresponding current flow and the corresponding rate of solution or corrosion of iron.

However, if the only ions present were those of a calcium bicarbonate solution rather than sodium chloride, the calcium cations would be attracted to the cathode and the bicarbonate anions to the anode (see figure 1b). Thus, at the cathode there would be a calcium hydroxide solution, and at the anode, a ferrous bicarbonate solution, part of which by reaction with dissolved oxygen forms insoluble ferric hydroxide and carbonic acid. Carbonic acid is a much weaker acid than hydrochloric acid. In fact, the combination of carbonic acid and bicarbonate ion serves as a 'buffer'

to prevent an excessive reduction in the pH at this point.

At the cathode of this system the calcium hydroxide reacts with the calcium bicarbonate of the main body of the water. As these mix together, they form insoluble calcium carbonate that when deposited on the cathode surface, develops a thin layer of limestone and serves as an insulator. One asset of this is to resist the passage of ions and current. Another asset would be a deposit of calcium carbonate which resists the diffusion of oxygen to the metal surface. In contrast, at the anode, the ferric hydroxide, usually with some underlying magnetite, offers little resistance to ionic movement and current flow.

In natural waters, sodium chloride and calcium bicarbonate seldom occur alone without the other. Various proportions of calcium bicarbonate and sodium chloride (and other minerals) may be present, so it is not surprising that different waters vary in their tendency to corrode and in their capacity to hinder or prevent corrosion.

It is evident that reactions at the metal interface are critical, and the general mineral quality of the water has a direct influence upon these reactions. High ratios of bicarbonate to chloride and of calcium to sodium are conducive to inhibition and protection.

Critical, also, is the rate of diffusion of oxygen to the interface. Dissolved oxygen has no electrical charge, and therefore is not ionized. It is used up, however, in the oxidation of the ferrous ion at the anode, and in the formation of hydroxyl ions at the cathode. These uses tend to deplete the oxygen at both electrodes, and thereby attract oxygen from the main body of the water. This diffusion to the metal surface is slow and controlled in part by the concentration of oxygen in the main body of the water. The greater the concentration, the greater the rate of diffusion to the surface.

When ferrous ions are contained at the anode by deposits of ferric hydroxide, the oxygen that diffuses to this area is used up in oxidizing ferrous ions to ferric hydroxide before it can get to the anode surface. This surface area is therefore devoid of oxygen. At the cathode, oxygen does get to the surface, and the rate of diffusion helps to govern the rate of corrosion when there is little or no calcium. But with sufficient calcium present, a tightly adherent deposit of calcium carbonate resists the diffusion of oxygen to the metal surface, and the corrosion rate is reduced accordingly.

Effect of pH

In 1924 Whitman, Russell, and Altieri³ concluded from careful experiments with Cambridge, Massachusetts, water that, in the pH range 4.1 to 10.0 at 22°C and 4.3 to 9.0 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 Baylis⁴ in 1926. He demonstrated the practical value of calcium carbonate protection by controlled pH and by 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.

Effect of Flow Rate

Another factor controlling the rate of diffusion is the velocity of flow of the water in pipes. With slow laminar

straight-line flow, the gradient from high concentration of oxygen in the main body to low concentration near the surface may be quite flat, so that the rate of diffusion is slow (figure 2a). With increasing turbulence, the laminar-flow layer adjacent to the pipe wall becomes thinner and the gradient steeper over the shorter path (figure 2b). Therefore, in corrosive waters, turbulence at higher flow rates permits oxygen to reach the cathode surface more rapidly, and the corrosion rates are accordingly greater.

However, with relatively noncorrosive, balanced waters with high ratios of calcium to sodium and high alkalinity, the higher flow rates also increase the concentration gradient for diffusion and decrease the distance that calcium and alkalinity must travel to the cathode to form and deposit calcium carbonate. This decreases the corrosion rates. It would appear that the higher the ratio of calcium and alkalinity to dissolved oxygen, the greater the protective tendencies of the water.

From corrosion prevention experience, it is well known that, to protect metals under conditions brought about by *stagnant* water, highly excessive inhibitor concentrations must be used. Such conditions often dictate the use of cathodic protection for corrosion prevention.

It has been an accepted fact that, where flow rates are low, dead ends are often the most troublesome areas in distribution systems, with regard to tuberculation and red water, and often, tastes and odors. The reasons for the difficulty are the long time of contact, which causes the accumulation of iron resulting from corrosion, and the fact that the protective ingredients in the water are not able to react at the point of corrosion and on the surface of the metal because of the low diffusion gradient at idle or low flow rates. The thickness of the laminar layer limits the rate of diffusion of ions to the pipe surface.

The concept of employing mechanical means to bring the protective ingredients to the pipe surface and thus to the reaction products of corrosion was suggested in 1959. Larson⁵ and Larson and Skold⁶ have shown that velocity (rate of flow) enhances tuberculation at 0.2 fps and calcium carbonate protection at 2.0 fps in Champaign-Urbana tap water (figure 3). Baylis⁷ in 1953 also showed the effect of velocity. McCauley⁸ gives strong weight to this factor. Eliassen et al.⁹ in 1956 related corrosion rate to velocity for a water with a negative saturation index. They indicated that the increasing velocity decreased the path of diffusion of oxygen through the laminar flow layer adjacent to the pipe wall. The oxygen in this nonprotective water thereby accelerated corrosion.

For a water with sufficient protective characteristics, the effect of oxygen can be nullified, or made to *contribute to the protective action*, when the thickness of the laminar layer is reduced.⁵ This thickness δ is related to velocity V and arbitrarily to the friction factor f by:

$$V\delta/\nu = 32.8/\sqrt{f}$$

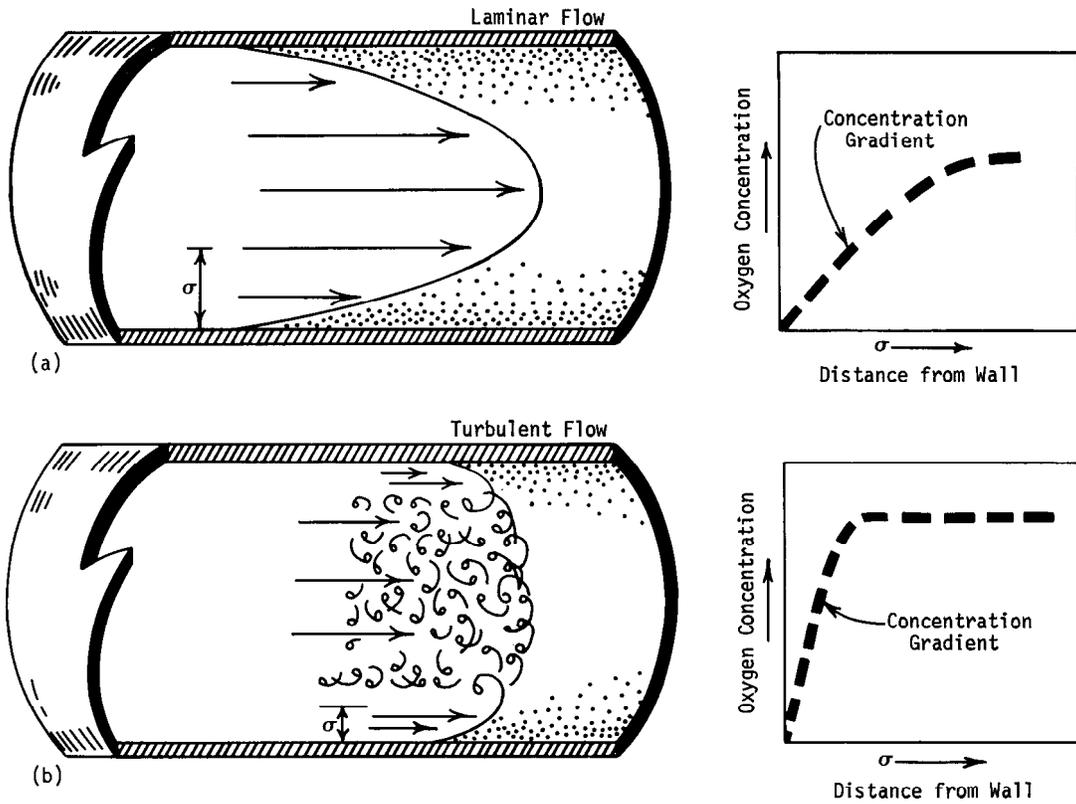
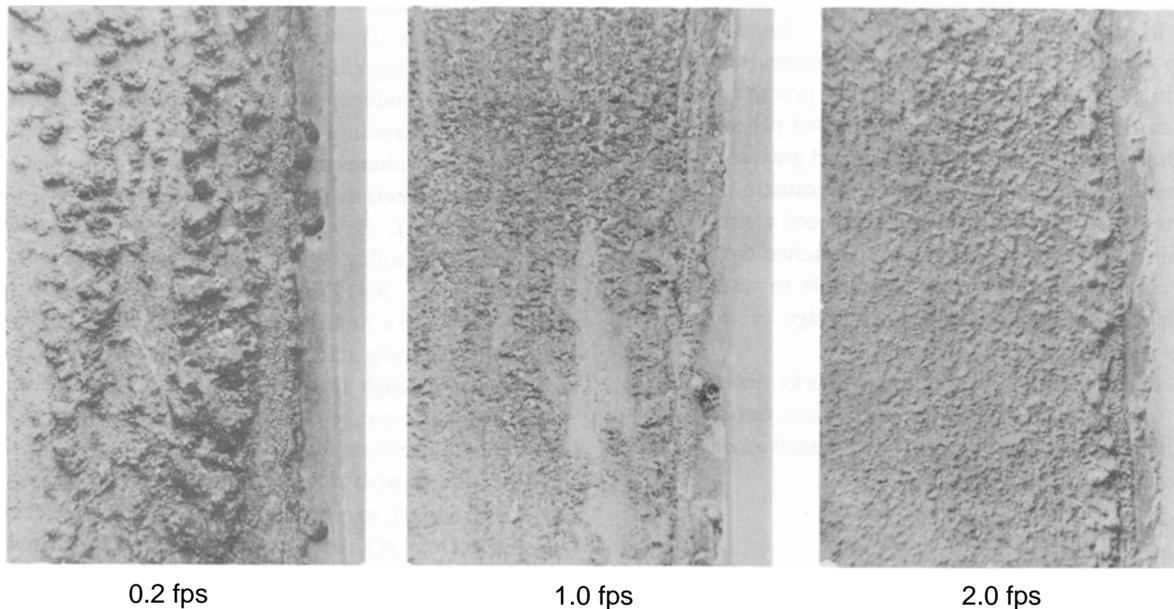


Figure 2. Comparison of oxygen diffusion under laminar and turbulent flow

and therefore, in turn, related to the Reynolds number, VD/ν (figure 4). D is the diameter; ν , the viscosity. Because the Hazen-Williams coefficient, C , is normally used by water utility investigators to establish roughness of pipe and

is determined from the same measurements of velocity and head loss, the relationship between the Reynolds number and the Hazen-Williams coefficient is introduced to indicate the laminar thickness at various velocities. In water supply



0.2 fps

1.0 fps

2.0 fps

Figure 3. Effect of velocity on tuberculation

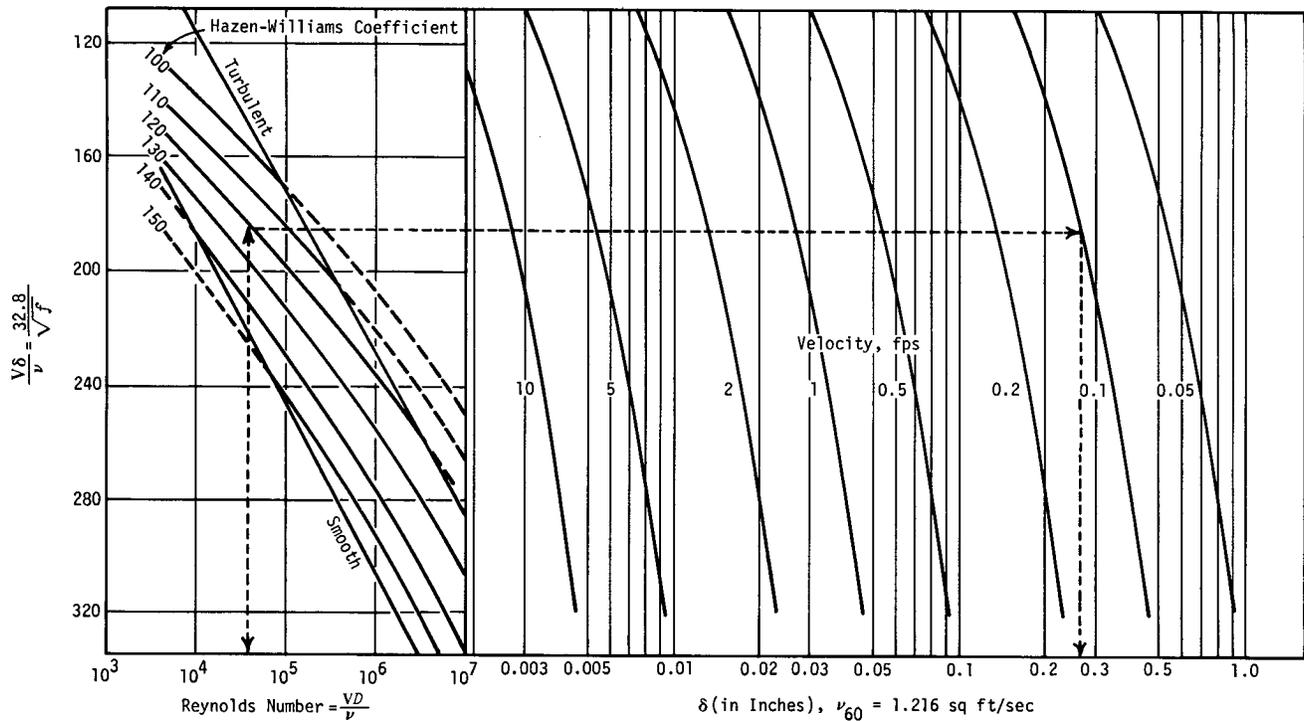


Figure 4. Relationship of laminar flow, layer thickness, friction, and Reynolds number

practice, the range of turbulent pipe flows is usually considered to be between the limits for perfectly smooth pipe and limiting velocities beyond which there is complete turbulence – that is, no change in friction factor. The Hazen-Williams coefficient has been plotted in figure 4 for a velocity of 4 fps, but there is very little difference in the position of the curves at other velocities.

It will be noted that the velocity of flow plays an important role with regard to the thickness of the laminar flow layer, which is decreased by approximately half as the velocity is doubled. It will also be noted that this thickness is greater for smooth pipe than for rough pipe. For instance, with a coefficient of 145 for the example indicated in figure 4, the thickness would be approximately 0.32 inch, which indicates the greater need for higher velocities at new installations. This, in part, may explain discrepancies in observed tuberculation at various locations in the same community .

Figure 4 does not show the effect of temperature. Temperature affects the viscosity ν , which, in turn, may increase the thickness of the laminar layer by approximately 30 percent as the temperature decreases to 35°F.

An example of corrosion inhibition by the combined application of calcium carbonate stability and velocity was demonstrated at a community which had suffered from red-water problems for nearly 25 years.¹⁰ The system was designed for fire flows greater than 500 gallons per minute (gpm), but the daily demand was only approximately

12,000 gallons per day (gpd). The maximum demand velocity in the residential area was about 0.04 fps in 6-inch pipe, which is a flow rate in the laminar range of the Reynolds number. Induced circulation at 60 gpm helped alleviate the distribution system problem, but data showed that corrosion continued until pH adjustment to a +0.3 saturation index eliminated the problem. When the induced velocity was reduced to 30 gpm (0.4 to 0.9 fps), a saturation index of approximately +0.6 was necessary to avoid corrosion by this water, which was softened to 90 mg/l hardness by ion exchange.

Although the principle of calcium carbonate stability is the one most widely applied and found to be most widely effective in treatment for the protection of distribution systems, there are many notable exceptions to this principle. A review and evaluation of this principle is warranted.

CaCO₃ Saturation Index

The equation for the saturation index was derived by Langelier:¹¹

$$I = \text{pH} - \text{pH}_s = \text{pH} - K + \log \text{Ca} + \log \text{Alk}$$

in which I is the saturation index; pH, the actual pH; and pH_s , the pH at saturation with CaCO₃. K is the $\log K_s/K_2$ (K_s and K_2 are thermodynamic constants, corrected for ionic strength and temperature).

The equation may also be expressed as:

$$\text{antilog } I = (\text{Ca})(\text{Alk})/K'(H^+) = H_s^+/H^+$$

in which K' is the antilog of K . These relationships exist:

$$\begin{aligned} \text{If } I &= 0; & \text{antilog } I &= 1.0 \\ I &= +0.4; & \text{antilog } I &= 2.5 \\ I &= +1.0; & \text{antilog } I &= 10.0 \end{aligned}$$

Another way of using this index is to relate the actual pH to the imaginary calcium and alkalinity concentrations that would exist if the actual concentrations were decreased by equal amounts (x) until equilibrium existed with the actual pH. Then:

$$I = \text{pH} - \text{pH}_s = K - \log(\text{Ca} - x) - \log(\text{Alk} - x) - K + \log \text{Ca} + \log \text{Alk}$$

Then the antilog of I would be:

$$H_s^+/H^+ = (\text{Ca})(\text{Alk})/(\text{Ca} - x)(\text{Alk} - x)$$

from which x , the initial excess, can be calculated. This method of calculation indicates a temporary excess but not the ultimate or equilibrium excess, which is always smaller. Ryznar¹² emphasized the importance of the concentrations of calcium and alkalinity to scale-forming properties:

$$\begin{aligned} \text{Ryznar index} &= 2\text{pH}_s - \text{pH} \\ \text{or} &= 2K + 2(\log \text{Ca}) + 2(\log \text{Alk}) - \text{pH} \\ \text{or} &= H^+/(H_s^+)^2 = (\text{Ca})^2(\text{Alk})^2/(K')^2 \end{aligned}$$

Ryznar stated that the scale-forming tendency increased as the index decreased from 6, or as the ratio of $H^+/(H_s^+)^2$ decreased from 10^6 .

McCauley¹³ proposed a driving force index (DFI):

$$\text{DFI} = (\text{Ca}^{++})(\text{CO}_3^{--})/K'_s \times 10^{10}$$

with which he estimates the carbonate ion concentration from the alkalinity, pH, and K'_2 .

All of these approaches recognize a weakness in the saturation index as a direct criterion of the magnitude of excess calcium carbonate. Incidentally, Langelier never intended it to be such a criterion, other than as a relative indicator that was subject to interpretation. Langelier¹¹ emphasized that the index "is an indication of directional tendency and

of driving force, but it is in no way a measure of capacity."

Caldwell and Lawrence¹⁴ established curves from which the equilibrium excess calcium carbonate could be determined for water at temperatures of 25 and 100°C. These curves are not entirely adequate for waters at lower temperatures, but they are helpful because interpretations for other temperatures can be derived.

The relative excesses of calcium carbonate at 25°C (77°F) are shown in figure 5 for equal calcium and alkalinity concentrations.⁵ This is perhaps the best numerical indicator of the available calcium carbonate that may be expected from supersaturated water and is similar to the momentary index reported by Dye.¹⁵ The reaction rates, however, are still dependent on: 1) temperature, 2) the influence of OH^- and H^+ developed at cathodic and anodic areas of the corroding surface, and 3) the buffering effect of greater concentrations of both calcium and alkalinity in the water. This buffering effect might be considered as the ability to maintain a potential or latent protective concentration after the deposition of a unit of calcium carbonate. These data on excess calcium carbonate may be made more useful by the inclusion of a measure of the buffering capacity related to the concentrations of calcium and alkalinity.

Experience has shown that the greatest weakness in the saturation index occurs with waters of relatively low alkalinity and calcium. Such waters have a saturation pH greater than 8.0 to 8.3. For some waters, the saturation index may have to be +1.0 or more to establish the saturation pH for calcium carbonate. At this level the buffer capacity is at a minimum. At higher levels, recent literature also indicates the formation of complexes such as CaOH^+ , MgOH^+ , CaHCO_3^+ , MgHCO_3^+ , and soluble CaCO_3 and MgCO_3 . These complexes remove calcium and alkalinity (HCO_3^- , CO_3^{--} , and OH^-) from active concentrations of their normal form. Analytical procedures fail to distinguish between these forms; therefore, there is a need to establish equilibrium constants for these complexes. Similar constants are required for CaHSO_4^+ , MgHSO_4^+ , and soluble CaSO_4 and MgSO_4 . In each case a temperature coefficient for the constant is required.

EFFECTS OF CORROSION

Corrosion is a problem that has plagued water utilities for as many years as metallic pipes, appurtenances, and water-using facilities have been employed. Most annoying and frustrating to water utility personnel, and to the consumer, is the deterioration of a clear, palatable, and safe water produced with care at the water treatment plant that occurs between the outlet and the point of use. Research on corrosion in distribution systems has been sporadic for

over 50 years, with notable successes in developing concepts, in the development and proper use of materials of construction, and in applying better knowledge of treatment to produce less aggressive water quality.

The effects of corrosion in public water supply systems are varied and numerous. Ultimate destruction is rare, but pitting to the point of penetration can occur with poorly protected steel pipe. The major effects are related to dis-

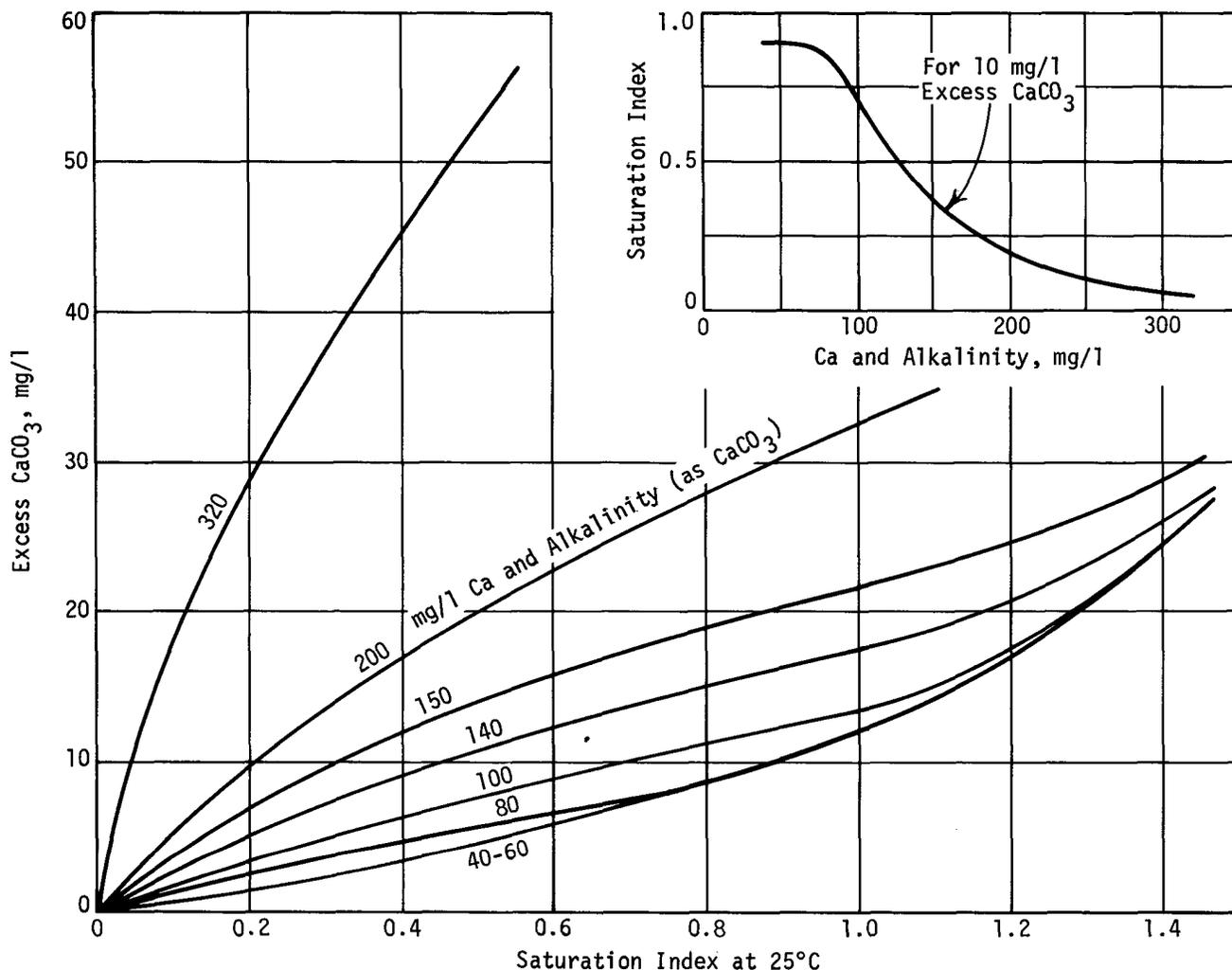


Figure 5. Excess calcium carbonate from supersaturated water

solution of iron and to tuberculation. For the past decade or two, cement lined water mains have been installed with increasing frequency, because of their excellent record of performance. However, thousands of miles of the older poorly coated pipe are still in service, and these are still subject to the effects of corrosion.

Rusty Water

One obvious result of corrosion can be the appearance of 'red water' at the household tap. This rusty water, resulting from corrosion, consists of hydrated iron oxide suspended as particles that cause the water to be turbid and unsightly. The rusty water stains household appliances and porcelain ware, and clothes laundered in such water are also stained. (Rusty water may also be apparent at the tap when the water supply source contains iron in excess. This is limited to some well water sources, and should not be mistaken for iron resulting from corrosion.)

Because distribution systems are designed to distribute water from one or more central sources to various areas and points of demand, the pipes are large near the source and become progressively smaller and interconnected toward the farthest points of demand. The larger mains usually carry a relatively sustained large flow of water, and the smallest carry erratic flows depending upon the number of points of demand. Minimal limits of size are built into the design to permit large flows for fire protection. Therefore, rusty (red) water as a result of corrosion is a lesser problem near the source than at the farthest points of demand. This is, in part, because the time of contact with the pipe per unit volume of water is relatively short for the larger mains, and longer for the smaller pipes where the demand is low or negligible for significant periods of time. Furthermore, as corrosion takes place and rust particles develop, they settle to the bottom of the pipe at periods of low or negligible demand, and are picked up and redistributed at periods of high or instant demand.

Tuberculation and Loss in Carrying Capacity

Another serious problem resulting from corrosion is evident as loss in carrying capacity of the water distribution system. When the corrosion products form nodules or tubercles on the interior surface of the mains or pipes, these protrusions offer resistance to the flow of water. This results in a decrease in flow rate, because the water pressure at the point of demand is reduced. This reduces or stops the flow of water at the tap in the taller buildings, and limits the rate of flow to the water hydrant for fire fighting. In order to overcome this reduced pressure or head loss, higher pumping pressures must be generated at the pumping station. Uncontrolled tuberculation can double the cost of pumping.

Cast iron pipe rarely fails structurally as the result of corrosion, but iron can be leached out from the iron-graphite matrix, leaving the graphite in a dense porous form. However, the rate of leaching by corrosion decreases as the penetration proceeds. Such corrosion is called graphitization, and becomes serious only with highly mineralized water which is rarely used for public water supplies.

Because loss in carrying capacity is associated with the 'roughness' of the interior of the pipe, it is important to differentiate between the different types of roughness that may develop :

- 1) The slime deposit or growth of bacteria, whether or not manganese or iron is present, can occur over the entire surface of the main.
- 2) Deposits of silt from untreated water is not uncommon in old mains or those operating under conditions of low flow. Such old depositions are known to be present even where water clarification has been practiced for over 20 years. In addition to sand, samples have been found to contain aluminosilicate clays and microorganisms. The effect of these deposits on carrying capacity is probably only slightly greater than that which calculations would indicate from the reduction of the pipe cross section.
- 3) Incrustation, or the formation of a crust over the metal surface, may be of various kinds, such as a) tuberculation in the form of nodules or spicules, resulting from localized corrosion; or b) after-precipitation or uniform deposition (not always a hard crust) of insoluble water constituents on the pipe wall.

Corrosion products also retard heat transfer for heating or cooling water, and therefore an excessive amount of water is required to provide the heating or cooling that is desired.

In addition to water distribution systems, the water used for domestic, industrial, and institutional purposes can cor-

rode the pipes of galvanized iron, copper, copper alloys, aluminum, and steel (see page 14). The choice of construction materials for other water uses may also be critical. Often there are alternatives. For different qualities of water and specific uses, one metal may be less subject to corrosion than others. Each metal or alloy has its limitations depending on the use and the quality of the water.

Chemical Treatment

Because water quality is implicated in the problem of corrosion, attempts have been made for over 70 years to alter the quality by chemical treatment. However, chemical control usually must be considered as a supplement to proper choice of materials and protective coatings, not as a substitute. Chemical control cannot be expected to overcome improper flow conditions, poorly designed distribution systems, defective materials, grossly faulty coatings, and under-design of copper pipe.

Chemical control involves expense and constant surveillance. The chemicals are costly, require proper feeders as well as storage, and must be carefully selected. They can be hazardous to personnel if handled carelessly. Analytical tests must be made at regular intervals to ensure proper application and to evaluate performance. None of these problems are insurmountable, however, and as more is learned about chemical control, its role should become increasingly important.

On the whole, chemical control has been more successful with water for industry than with water for drinking. In many industrial processes, chronic or acute toxicity is not generally a significant factor, and therefore there is no serious restriction in kind and quantity of chemical control. Because the water is not used for drinking or other household or institutional purposes, high concentrations of inhibitors, such as chromates, nitrites, phosphates, organics such as tannin, and synthetics such as mercaptans can be tolerable and, when quantity requirements are low, economical.

For example, chromates, phosphates, and organics have been used in relatively large quantities with exceptional success in treatment of cooling waters cycled through heat exchangers and cooling towers. Preheaters with oxygen scavenger chemical treatment and pH adjustment are also effective and are economic assets to boiler feedwater control. With water for drinking, however, there are serious limitations on kind of chemicals used, because of effects on taste, odor, color, turbidity, and toxicity, and almost equally serious limitations on quantity, because a great volume of water must be supplied at low cost and the water once used is not recycled.

WATER SURVEY LABORATORY STUDIES ON CORROSION

The literature abounds with unsubstantiated observations on corrosion without data. How often are conclusions published without data on time of exposure, stress, stray currents, composition of the metal or alloy, the quality of the water environment (pH, temperature, dissolved oxygen, mineral analysis), concentration of inhibitor, rate of flow, and a host of other variables such as trace elements, potential for presence of copper, galvanic action, or turbulence?

It is one thing to study the literature on corrosion testing and another to try to extrapolate the findings to apply to specific problems. Therefore, it is necessary to conduct laboratory studies under controlled conditions to evaluate the relative effects of primary variables as a basis for extrapolation for specific applications. The following studies have been directed largely to evaluate the mineral quality variables on corrosion, and to determine the effects and demonstrate means for reducing corrosion.

Needless to say, research on corrosion involves many measurements for controlled conditions over a significant period of time. In one 10-month period, over 500 specimens were used for approximately 45 series of tests, during which about 4000 operations such as cleaning and weighing specimens and quality control tests were made. Over 16,000 current and voltage readings accompanied these tests.

Simulating the normal (real life) corrosion rate of metals in the laboratory is important. By design, metals in normal conditions are exposed for many years. The time element in laboratory studies is much shorter. It is well known that at first exposure, metals in laboratory experiments corrode at a very high rate. Depending upon variables contributing to acceleration and inhibition, the first exposure rate decreases to a constant or equilibrium rate which may require 50 to 100 days to achieve. This equilibrium rate is the one closest to normal exposure.

At first a major problem for all corrosion studies was the necessity for destroying the specimen to determine the corrosion rate. This could involve many specimens to determine the equilibrium rate. The problem was overcome by the observation of Ronald Skold¹⁸ that during polarization tests at low applications of current to the specimens, the change in the potential of the specimens was high for high corrosion rates, and low for low corrosion rates. Because the required current density was in the microampere range for only a few minutes, the specimen was not destroyed, and it was possible to develop an empirical relationship between the instantaneous corrosion rate and the change in potential per unit of applied current density. Within a few years after the publication of this discovery^{17,18} the theory and improved application of this technique were developed by many investigators in the field, to the point

that the application of this finding to corrosion research expanded at an exponential rate.

This section on laboratory studies begins with some preliminary studies conducted by the Illinois State Water Survey on corrosion of steel, followed by our studies with cast iron, and with water quality parameters such as chloride, alkalinity, calcium, and pH.

Qualitative Studies on Ion Migration

In 1948, a preliminary investigation was begun to obtain qualitative data on the water composition at the cathode and the anode, as affected by waters of different mineral compositions.¹⁹ 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 5×6-inch electrodes were located at opposite ends of an electrolysis cell divided into nine 270-ml compartments by vertical, parallel, porous alundum plates (figure 6).

University of Illinois 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 2.

Progressive quality changes occurred in each compartment with increasing milliampere-hours of current con-

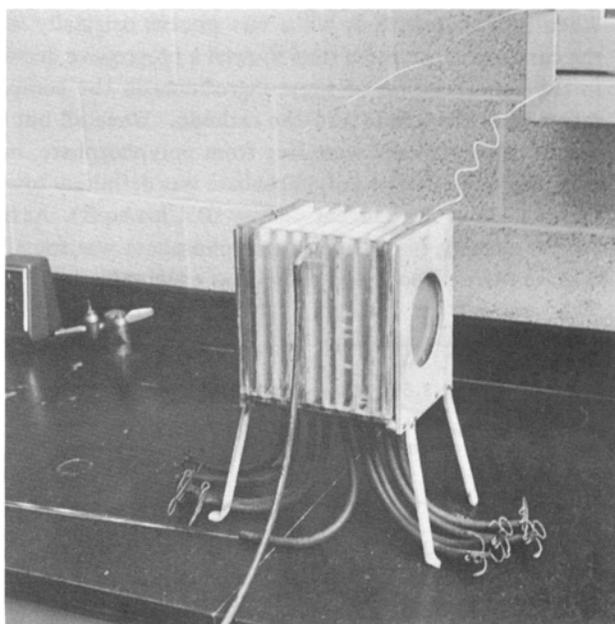


Figure 6. Experimental corrosion cell

Table 2. Tap Water Composition

	mg/l	me/l
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 (degrees Fahrenheit)	55	
pH	7.4	

sumption. The changes were particularly significant in the end compartments at the electrodes.

The increase in pH at the cathode is shown in figure 7 at three current densities (cd) 0.9, 1.7, and 3.5 milliamperes per square foot (ma/sq ft), and the accompanying reduction in calcium and magnesium (me/l) is shown in figures 8 and 9. At low current density, the pH was not affected so greatly for equivalent milliampere-hour values, and, accordingly, magnesium precipitation was minimal.

The general distribution of calcium, magnesium, and alkalinity concentrations (me/l) in the various compartments is shown in figure 10. The considerable 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/sq ft). At high current density (4 ma/sq ft), polyphosphate was found to migrate toward anode and cathode at equal rates.

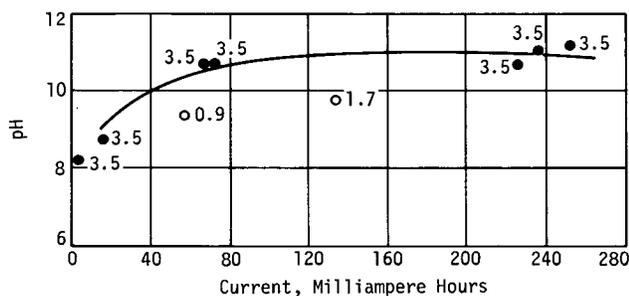


Figure 7. pH at cathode

It would have been interesting to continue these tests with water containing bicarbonate and more chloride, but it was decided to use a different approach in order to study the influence of bicarbonate and carbonate ions on corrosion rates.

Immersion Tests with Steel Specimens

Because almost all natural waters contain bicarbonate 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. Borgman²⁰ 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 Evans²¹ in 1927. Mears and Evans²² 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 but was different for the various proportions. Therefore, pH as well as the carbonate ion variables affected the results.

Apparatus of the standard type²³ for total-immersion tests of nonferrous metals was constructed for the Water Survey studies and is shown in figure 11. The 1½x3 inch triplicate specimens of 0.01-inch '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 percent solution of HCl and HNO₃ for 2 minutes; placed in concentrated HCl for 1 minute; rinsed in

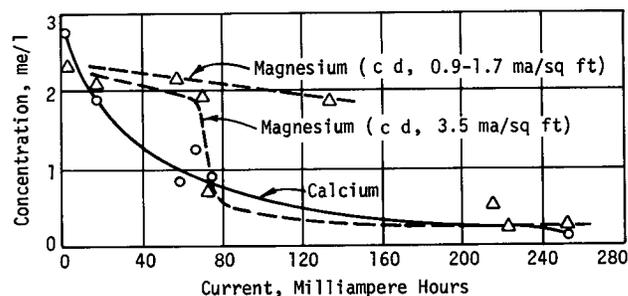


Figure 8. Magnesium and calcium concentration

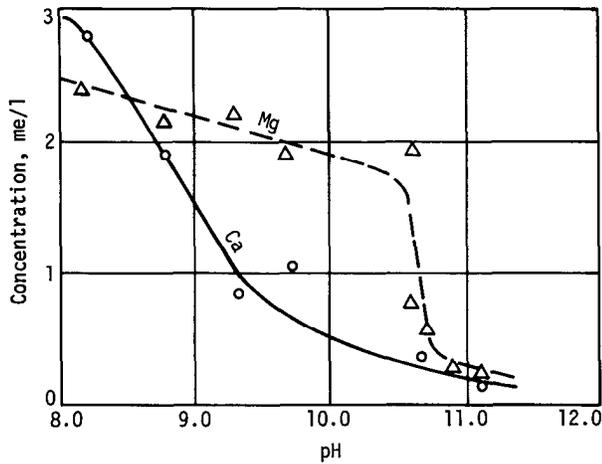


Figure 9. pH and concentrations at cathode

acetone; and dried and weighed 48 hours 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. The ratio of surface area of the specimens to volume of water was 3 square centimeters per liter. The specimens were suspended from a bar that was mechanically rotated in a vertical plane to move the submerged specimens in a similar vertical plane and produce an equal velocity on all points of the surfaces. A low velocity was deliberately chosen in order to simulate the conditions usually existing in as much as 25 to 50 percent of any municipal distribution system, including service lines.

Various proportions of sodium bicarbonate and chloride, sodium bicarbonate and sulfate, and sodium bicarbonate and nitrate were used at pH 7 and 9. The water was continuously aerated, and carbon dioxide was continually bubbled through the water to adjust and control pH. The results are shown in figure 12.

It was noted that, after the proportion of sodium chloride or sulfate reached a given value, a corrosion rate of from 100 to 125 milligrams per square decimeter per day (mdd) 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 mg/l dissolved oxygen was present, the corrosion rate in this range may have been higher, particularly with increasing proportions of sodium chloride. It may be worthy to note that the highest ratio of chloride to alkalinity that did not corrode was about one half as much as the sulfate to alkalinity ratio.

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

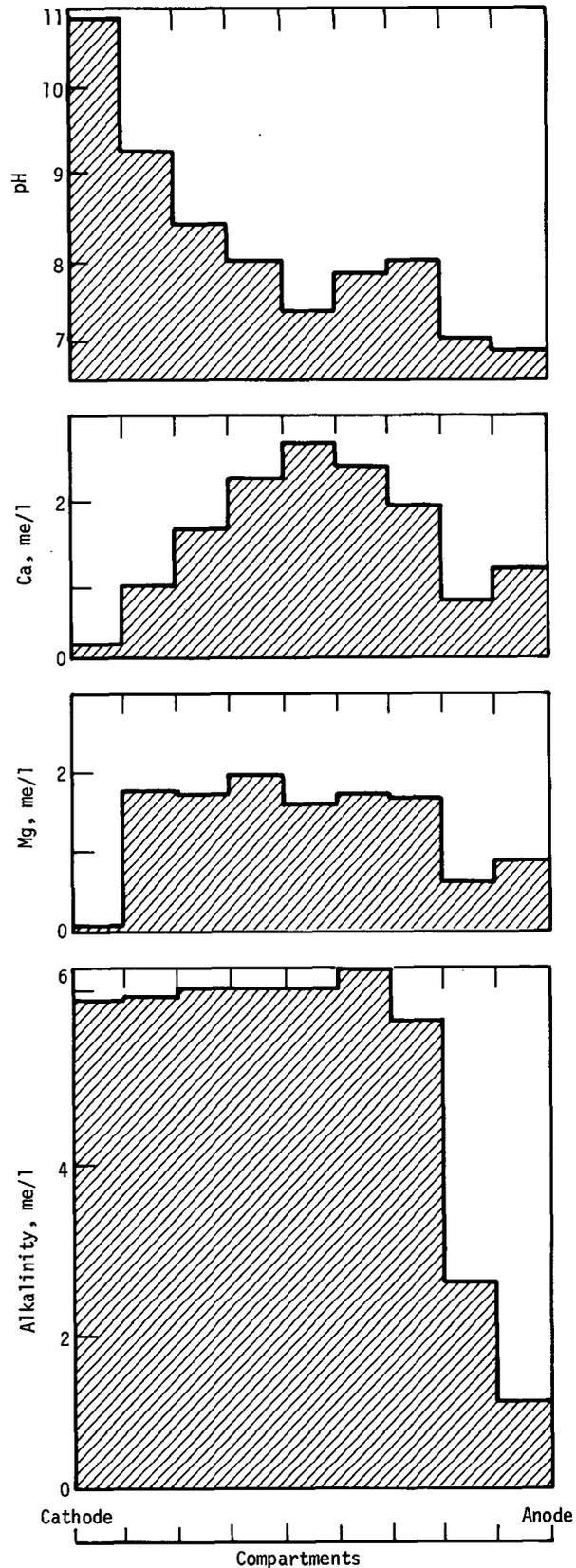


Figure 10. Concentration in compartments

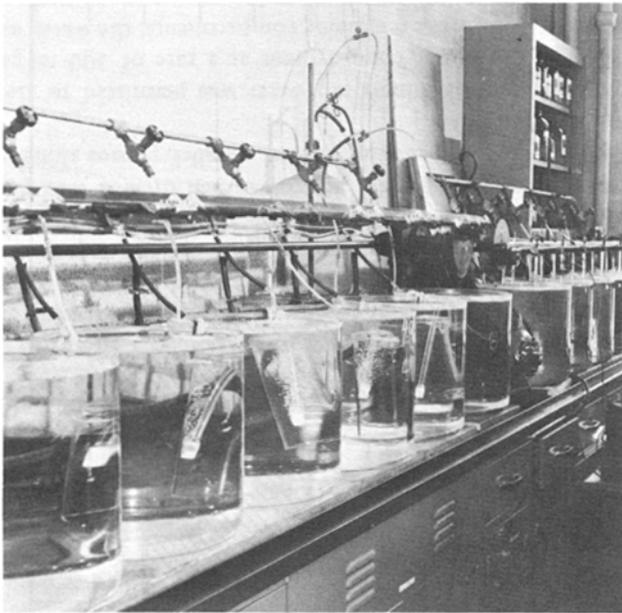


Figure 11. Total-immersion test setup

under the experimental conditions. For example, of three specimens in a solution in this range, one may have corroded at a rate of 10 mdd, and the other two 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 sensitivity and discontinuities of the surface of the specimen.

It was significant that, for any specific chloride or sulfate concentration, corrosion rates might be considerably greater for solutions of low total mineral content than for those of high total mineral content with appreciable alkalinity, a finding that is contrary to the usual predictions which forecast higher corrosion rates for higher mineral content.

Also, for some chemical compositions, corrosion rates appeared to be greater at pH 9 than at pH 7; however, for 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 were surprising. Although a water that contains only bicarbonate and nitrate is a rarity, it should be of interest to make a further study on 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 similar to those from the 3-day data.

These data are specifically limited to dissolved solids concentrations between 200 and 1200 mg/l, under the flow velocity and temperature conditions indicated.

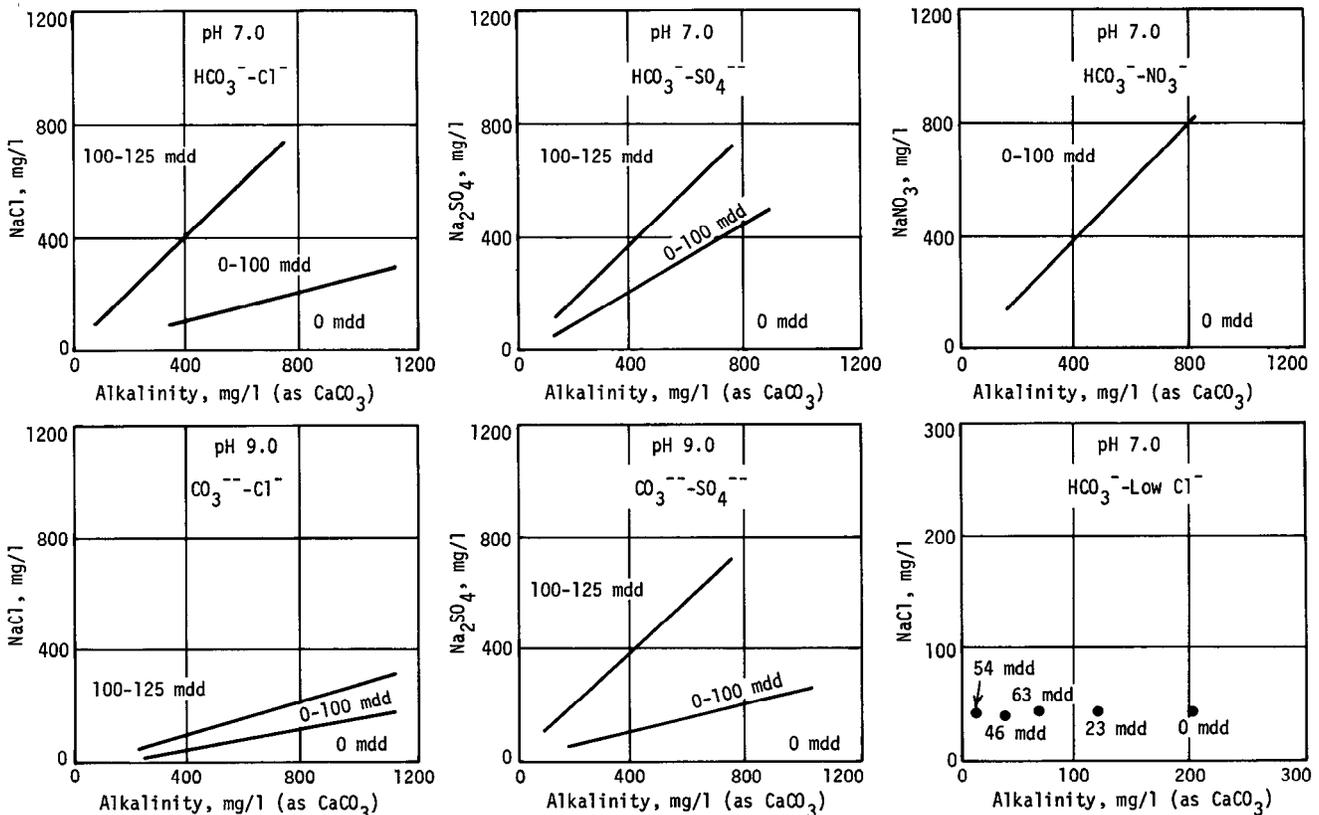


Figure 12. Results of total-immersion tests

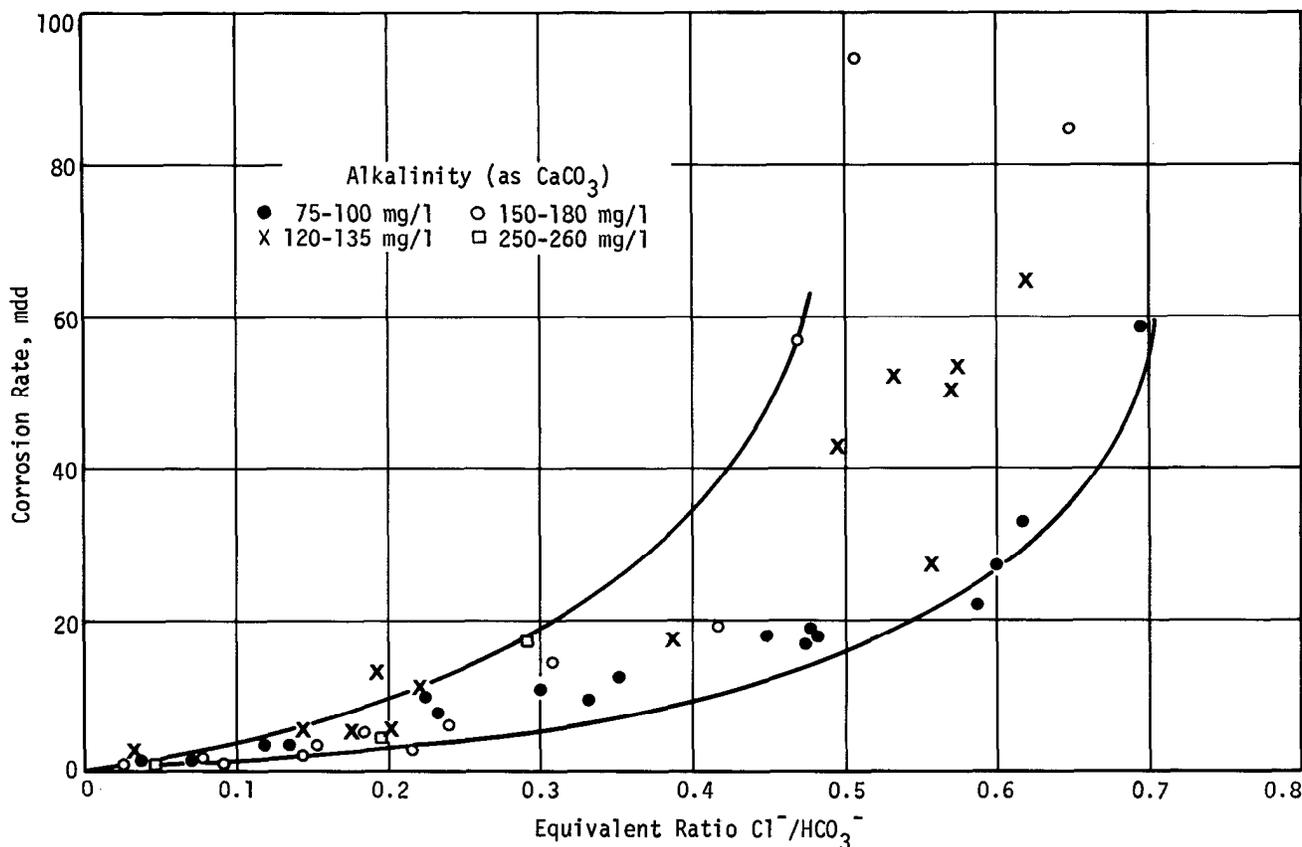


Figure 13. Effect of chloride-bicarbonate salts of sodium ratio on corrosion of mild steel

Figure 12, however, also shows the corrosion rates experienced in a test series in which the combined sodium chloride and bicarbonate concentrations ranged from 60 to 250 mg/l. 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 mg/l NaCl was present.

Extreme caution is needed in interpreting these data or applying 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. However, Mears and Evans²² have shown that pitting is less likely to occur where little

or no anodic inhibitor is present.

Further immersion studies with mild steel confirmed the conclusion that corrosion is accelerated by increasing proportions of chloride to bicarbonate. During this study¹⁹ considerable time was spent in evaluating various methods of preparing specimens, and it was found that very minor stresses imposed on the steel by lack of care in handling promoted excessive variability in results. Subsequent 3-day tests established a better corrosive-inhibitive relationship for various equivalent ratios of chloride-bicarbonate salts of sodium at pH 7, as shown in figure 13. The curves indicate the upper and lower boundaries of the observed corrosion rates. This figure would appear to indicate that even small proportions of chloride to alkalinity cause some corrosion.

From these data it appears that increasingly high rates of corrosion occur as the chloride to bicarbonate ratio increases, particularly above a value of 0.3. This proportion approximates the proportion of chloride plus sulfate to bicarbonate in Great Lakes waters and classifies²⁴ such water in a range which is sensitive to additional corrosives and probably to inhibitors.

C. H. Spaulding, in a preliminary unpublished study of this problem, suggested that free chlorine appeared to be responsible for excessive tuberculation. This and other work

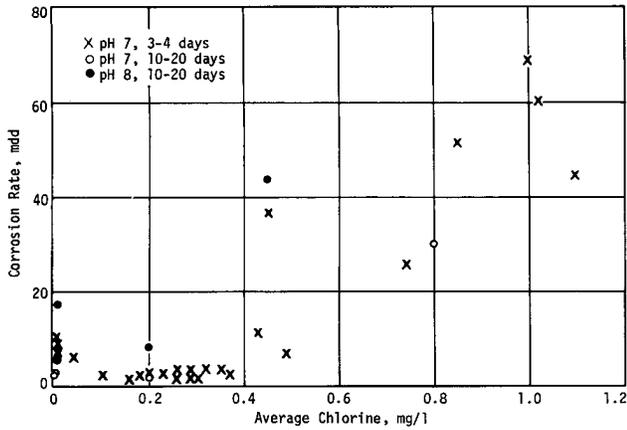


Figure 14. Effect of free chlorine on corrosion of mild steel

on the problem²⁵ prompted the undertaking of a number of tests to obtain a relative evaluation of this factor. These tests indicate (figure 14) that free chlorine in concentrations above 0.4 mg/l corrodes steel at room temperature in aerated water of about 120 to 135 mg/l alkalinity and about 30 mg/l sodium chloride, at pH 7 and 8, at low velocities.²⁴ In figure 15, these results have been superimposed on other data for corrosion rates with no chlorine added to indicate the relative corrosion rates at the particu-

lar chloride-bicarbonate ratio. Figure 15 also shows the results of tests of 3 to 6 days duration using chloramine in concentrations of 0.4 to 3.6 mg/l. These data suggest that corrosion is inhibited by conversion to chloramine.

It is probable that similar relative results would not have been obtained at other proportions of chloride to bicarbonate. If 5 mg/l sodium chloride had been used rather than 30 mg/l, a greater proportion of inhibitor would have been present and more than 0.4 mg/l chlorine may have been necessary for comparable corrosion rates. If 80 mg/l sodium chloride had been used rather than 30 mg/l, the additional corrosion induced by 0.4 to 1.0 mg/l chlorine may have been negligible. No additional studies have been made on other corrosives or inhibitors.

Tests have also indicated corrosion rates to be higher at pH 8.5 and 9.0 than at 7.0, 7.5, and 8.0. A twofold increase in corrosion rate resulted when the velocity was increased from 0.14 to 0.89 fps at pH 8.5 and 9.0 with 1000 mg/l alkalinity and 120 mg/l sodium chloride as shown in figure 16.

Minimum corrosion was noted at pH 7.0, 7.5, and 8.0 at both rates. Although high pH is normally considered an inhibitor, this apparent contradiction indicates a need to recognize alkalinity as a natural inhibitor in water. In the absence of calcium the high pH intensified incipient pitting.

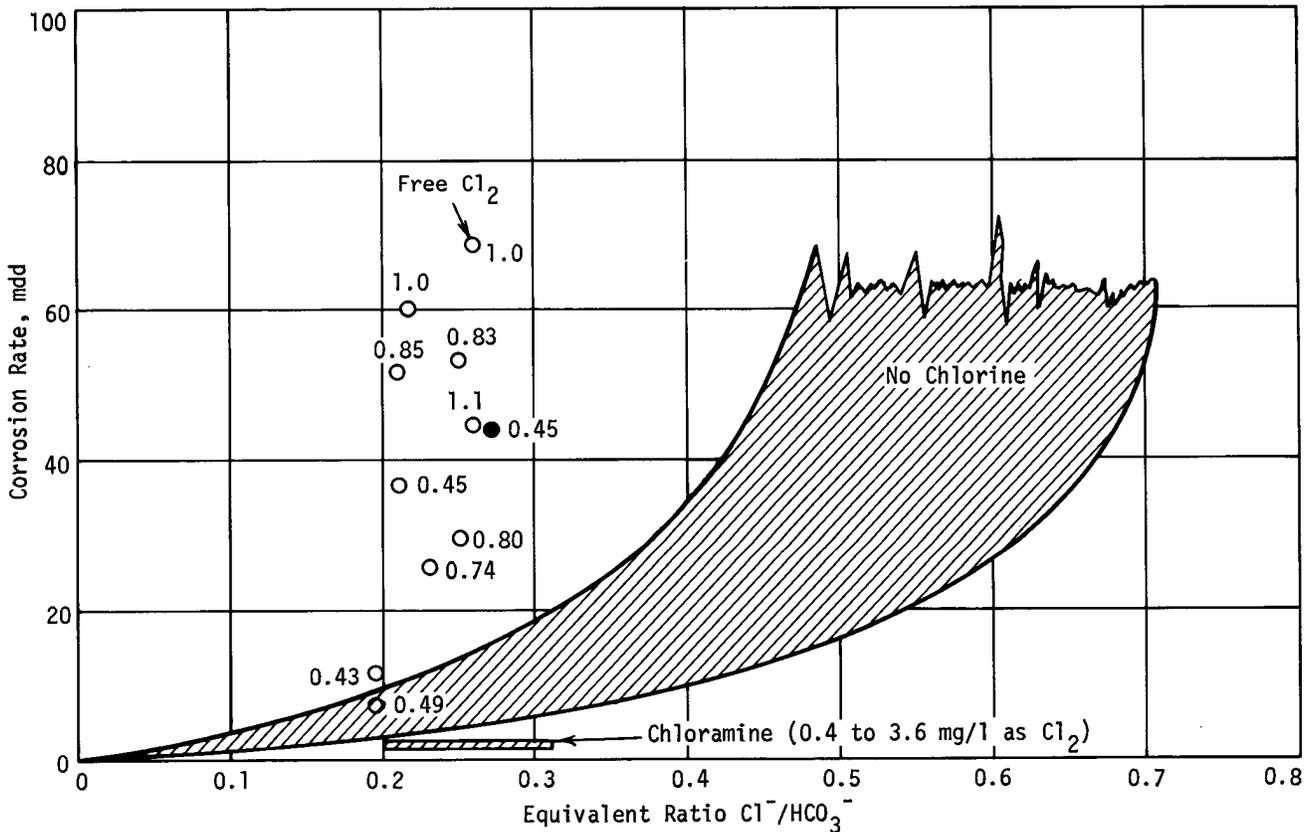


Figure 15. Relative corrosion rates at particular chloride-bicarbonate ratios with and without chlorine

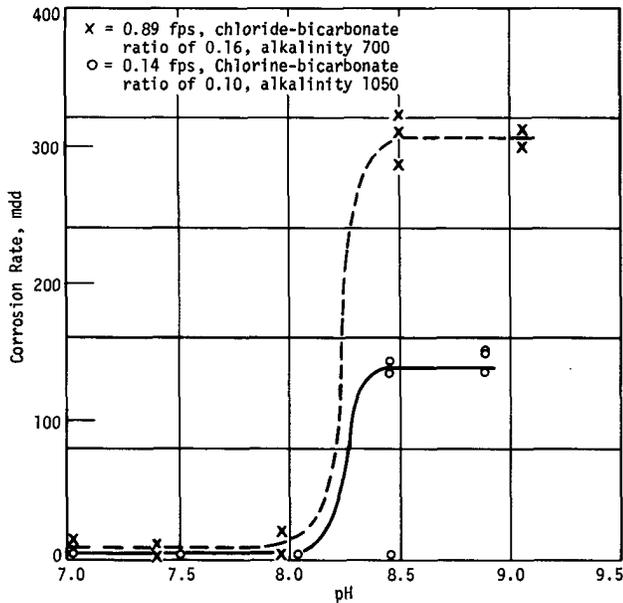


Figure 16. Effect on corrosion rates of increased pH and change in velocity

As previously mentioned, a new method for measuring corrosion rates on submerged specimens was developed in 1956.¹⁸ For the first time, rates of corrosion could be determined in a very short time without destroying the specimen. Thus, a single specimen would suffice for periodic measurements over an extended period of time.

The method consists of applying current to the specimen in micro amounts and measuring its change in potential

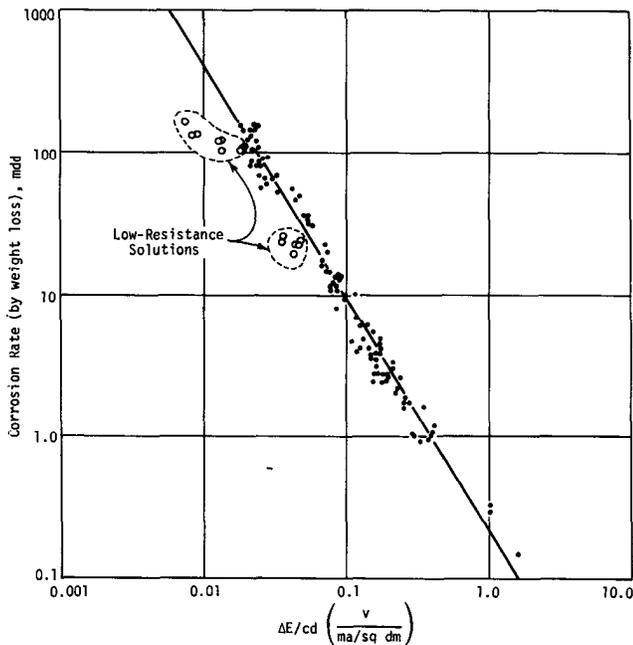


Figure 17. Empirical relationship between initial slope of polarization curve (resistance) and corrosion rate determined by weight loss

against a reference electrode. The change in potential per unit of applied current density ($\Delta E/cd$) was found to correlate quite well with weight loss measurements converted to milligrams per square decimeter per day as shown in figure 17. It is, in effect, a measure of film resistance on the metal surface.

This method was used to establish the data on the effect of pH on corrosion of steel in water of a specific quality (see figure 18). The curves indicate results after: A, 16 days; B, 12 days; C, 8 days; D, 4 days; and E, 2 days. Tests were made on an air-saturated solution with a NaHCO_3 content of 2.5 me/l, NaCl content of 0.5 me/l, temperature of 19 to 28°C, and a velocity of 0.14 fps. The rates of corrosion were confirmed by total weight loss of the specimens at the end of the test.

Figure 19 shows the results of a more recent test²⁶ with a water having a much higher chloride content than that shown in figure 18. 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 a low chloride content. Both of these tests were conducted at low velocities.

It should also be noted that the alkalinity was constant at all values of pH. The Whitman, Russell, and Altieri data³ were obtained with different concentrations of alkalinity and chloride at each pH (see page 7).

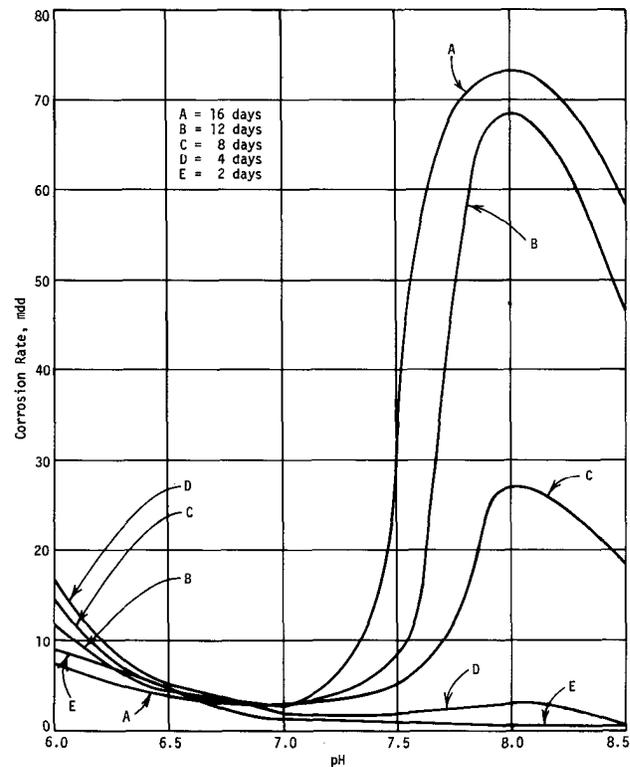


Figure 18. Effect of pH on corrosion rate at chloride-alkalinity ratio of 0.4

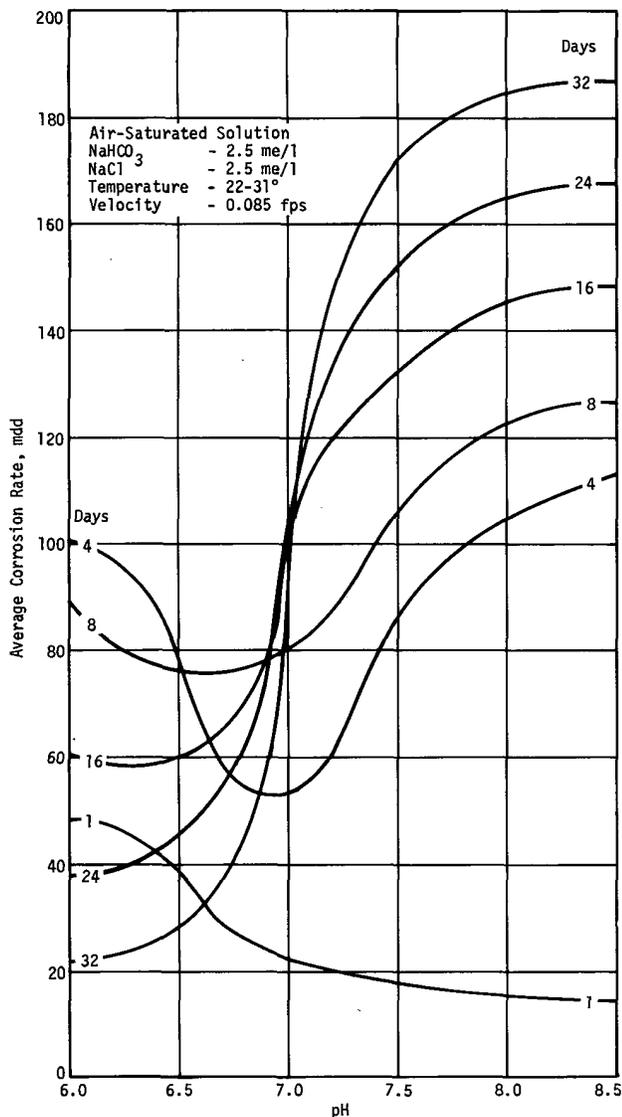


Figure 19. Effect of pH on corrosion rate with Cl/alk ratio of 1.0

Figure 20 shows the type of corrosion products adhering to the steel specimens used to obtain the data in figure 19. 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.

Significance of Corrosion Rate Measurement

When a corrosion rate is measured, it is usually reported in milligrams per square decimeter per day (mdd) or in terms of inches of penetration per year (ipy). The first is a weight measurement per unit surface; the second is the average depth measurement on the surface, calculated from the weight measurement. Therefore, $mdd \times (0.00144/den-$

sity) equals inches per year. The ipy measurement may also be made for the depths of pits on the surface. These can be related by considering no corrosion over part of the surface as the result of being cathodically protected by the remaining surface (the anode) which is corroding.¹⁶

When essentially no protection exists, there is a general uniform corrosion rate (figure 21). If part of the surface is not corroding, the remainder of the surface is corroding at a proportionally greater rate. Deep pitting or local penetration can take place when the surface is predominately cathodic, unless the corrosion products become so dense that the overall rate is reduced. Local points of tuberculation are associated with local points of pitting.

Mild Steel

These studies, in part, contribute to the following classification of waters which considers the mineral content, dissolved oxygen, and pH (acidity) relative to the effect on the corrosion of mild steel.

No Minerals – Dissolved Oxygen Present. In the absence of minerals, increasing pH decreases corrosion rates by water containing dissolved oxygen. However, if the pH is near, but not above, that required for complete protection, pitting occurs, which rapidly decreases the useful life of mild steel. Cavities at joints and welds and corners where circulation is poor, which do not permit oxygen to be maintained at the surface, are subject to localized corrosive attack.

Pitting takes place at local unprotected points of corrosion where the corrosion products prevent the diffusion of oxygen to the metal surface, thereby permitting differences in oxygen concentration at the metal surface. Similar pitting can occur under deposits of debris. Also, differences in oxygen concentration, as at the water line of surfaces exposed partly to air and partly to water, will cause pitting. The rate of corrosion increases at higher temperatures.

No Minerals – Dissolved Oxygen Absent. In the absence of dissolved oxygen, the pH of 'high purity' water confined

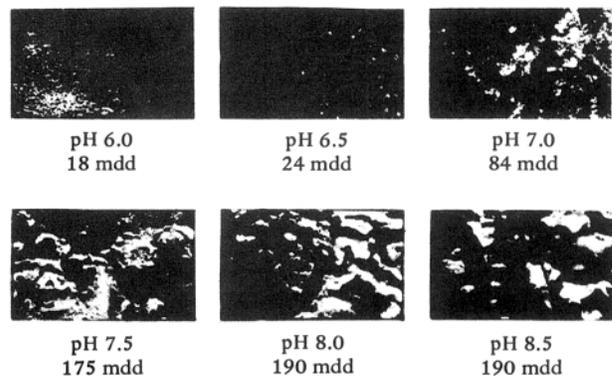


Figure 20. Corrosion products on steel specimens

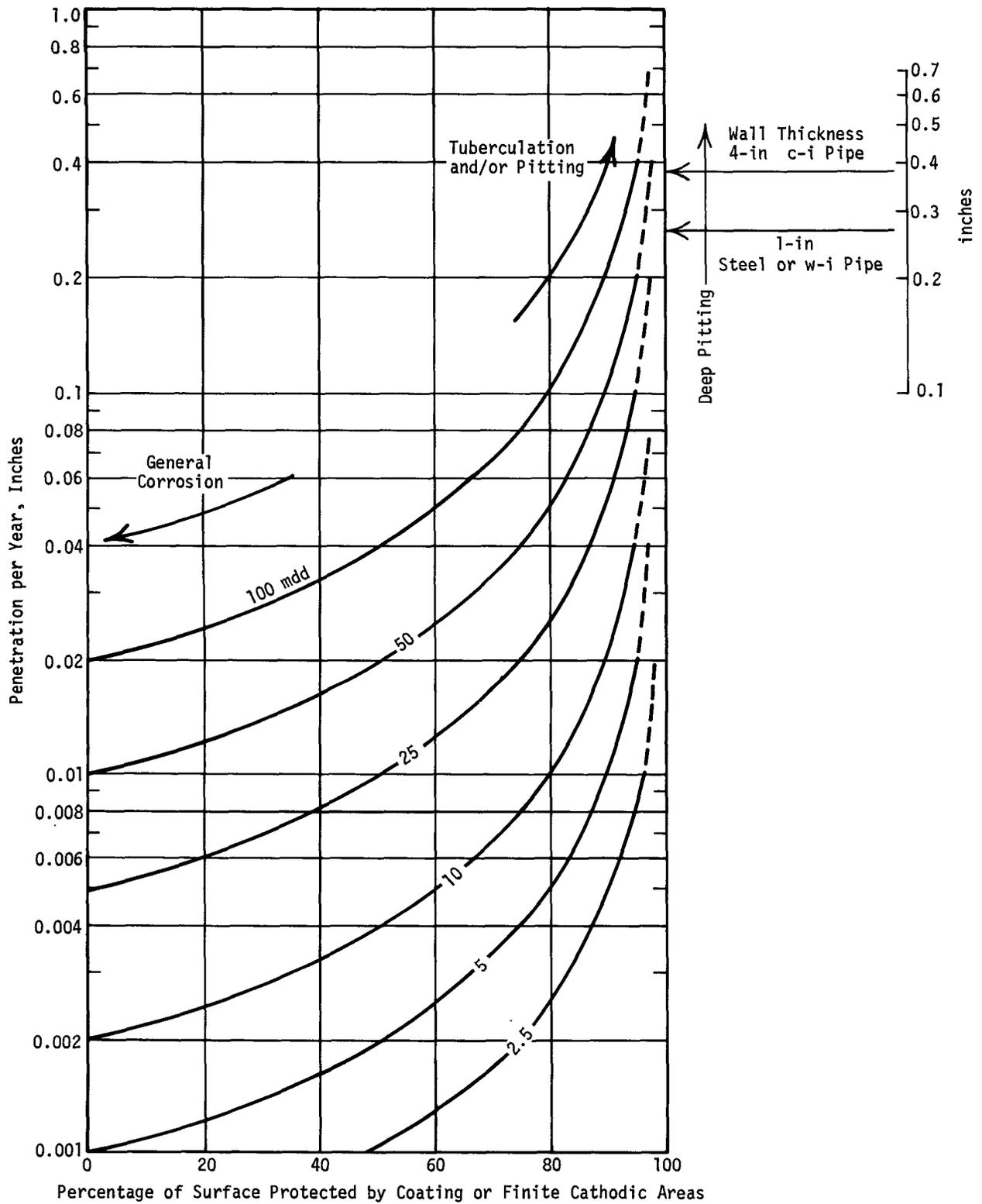


Figure 21. Relative corrosion rates with partial protection

in mild steel containers adjusts itself to about 8.4 and corrosion becomes negligible. However, all natural waters are mineralized to some degree.

Noncarbonate Minerals – Dissolved Oxygen Present. In the absence of carbonate minerals, increasing concentrations of other common minerals, such as chloride and sulfate salts, increase the conductivity and therefore the corrosion rate at all pH values below the pitting range of pH, and increase pitting when the pH is just below that required for uniform protection in the presence of dissolved oxygen. Increasing temperature accelerates both general corrosion and pitting.

Carbonate Minerals (No Calcium) – Dissolved Oxygen Present. Carbonate minerals, indicated by the alkalinity determination for bicarbonates, inhibit corrosion. They act contrary to the accelerating salts of chloride and sulfate in waters containing dissolved oxygen. In the absence of calcium, this inhibition is maximum at pH 6.5 to 7.0 in concentrations five to ten times above the chloride and sulfate salt concentration. Inhibition also is greater at increasing pH above 9. At concentrations decreasing five or ten times below the chloride and sulfate salts, corrosion rates increase. Since nearly all natural domestic waters or carbonate minerals contain alkalinity, and in addition usually contain chloride and sulfate salts, this too is a criterion in classification.

Minerals – Dissolved Oxygen Absent. In the absence of dissolved oxygen, the types of mineralization are less important with respect to useful life of mild steel. This is indicated by the following examples:

- 1) Plumbing experience indicates that properly designed hot water heating systems can be made of steel, provided that no water (domestic) is lost from the system; avoiding the addition of make-up water containing dissolved oxygen also prevents loss of corrosion products that inhibit the corrosion.
- 2) The useful life of steel used for feedwater heaters, boilers, and piping for power plants may be extended considerably by maintaining an oxygen-free boiler feedwater.

Calcium Salts – Dissolved Oxygen Present. From the standpoint of corrosivity, stability as indicated by saturation with calcium carbonate is the most widely accepted criterion in classification. Uncoated mild steel or machined cast iron requires a very significant supersaturation to form a visible deposit. This criterion has specific limitations:

- 1) A minimum alkalinity of 50 to 100 mg/l (calculated as CaCO_3) and a minimum calcium of about 50 mg/l (as CaCO_3) must be present at normal temperatures (32 to 160°F) for an extended life for the metal. Such water will require a pH much higher than the calculated pH of saturation.
- 2) The greater the concentrations of calcium and alkalinity, the greater the protective action of the water.

However, such increasingly high concentrations are responsible for an additional tendency to deposit objectionable quantities of scale at temperatures above that at which saturation stability is established.

- 3) The protective action is enhanced by movement of the water and decreases at near-stagnant conditions.
- 4) The protective action may be nullified at higher temperatures when the pH is high enough to deposit non-protective magnesium hydroxide.
- 5) Pitting and tuberculation will occur in the presence of dissolved oxygen if the stability and velocity are near, but still below, that required for complete protection.
- 6) The protective action is decreased by increasing proportions of chloride and sulfate salts above a ratio of about 0.1 or 0.2 to 1 with respect to alkalinity. This limitation becomes less significant in the absence of dissolved oxygen.

Cast Iron

Corrosion of cast iron is unlike that of steel. It appears that a great difference in susceptibility of cast iron to corrosion exists between 'as cast' or annealed cast iron, and machined specimens with no protective barrier.

Modern production of cast iron produces an outside surface of iron oxide, silicates, and aluminosilicates which serves as an excellent barrier to atmospheric corrosion, and usually to water. When this surface is ground to make it smooth or machined for fabrication, a surface containing graphite in a matrix of ferrite or pearlite is exposed. The graphite, which occurs at about 0.04 millimeter intervals, serves as cathodic points to stimulate an initial galvanic corrosion of the adjacent iron.

Grinding of Cast Iron Pipe Interiors. It was learned through 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.²⁶ In this process, most cast iron pipe interiors are ground to the extent that 10 to 50 percent of the surface consists of graphite in the ferrite or pearlite matrix.

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 unground 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 22 shows a microphotograph (magnified 50x) of an unetched mount.

When the hard 'skin' on the internal surface of the pipe was scraped off, the black phase between the metal surface

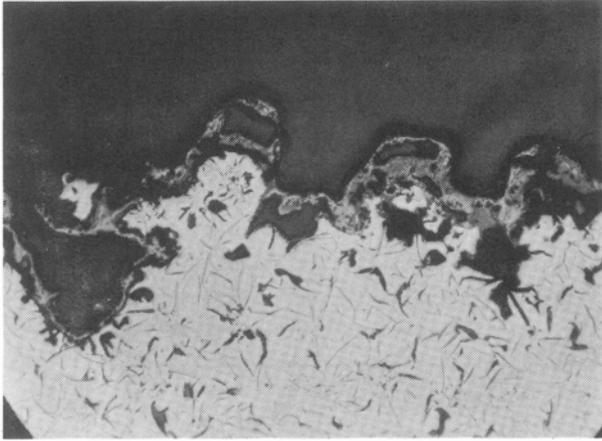


Figure 22. Microphotograph of an unetched mount of cast iron

(with black graphite particles dispersed in the matrix) and the gray phase was found to be ferromagnetic (Fe_3O_4) with a cubic structure.

The external 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 $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_2$.

This silicate skin, which is highly insoluble, appears to provide an effective barrier to corrosion by water. It is very brittle and therefore may not be a completely effective barrier when damaged.

Immersion Tests with Cast Iron Specimens. Laboratory tests were performed with cast iron in a manner similar to the tests for steel. The specimens were totally immersed in the water, saturated with air at room temperature, and with carbon dioxide used for controlling pH. The apparatus, as used with the steel immersion tests, provided a constant velocity of the specimen in a vertical circular path. Cast iron specimens were machined and abraded with No. 120 grit paper and degreased prior to use. At the end of the tests, the specimens were cleaned electrolytically for 5 minutes in 10 percent ammonium citrate prior to the determination of weight loss, in terms of milligrams per square decimeter per day.

Calcium Effects. With machined cast iron specimens in water containing calcium, an interesting overall average of the results is indicated in figure 23.²⁷ This broad generalization indicates that irrespective of the saturation index, of velocities from 0.08 to 0.85 fps, of minor variations in the chloride to alkalinity ratio, and of the presence or absence of chlorine, chloramine, or silica, the concentration of calcium in the presence of 125 mg/l alkalinity is a primary factor in the inhibition of corrosion of machined cast iron. It also shows that a certain length of time is required for effectiveness to become apparent. In this generalization rep-

resenting all tests, there are broad variations, as much as tenfold in some cases, for each level of calcium.

For the following specific modifications in water quality, the data are represented as smooth lines from the average rates determined five times per week for triplicate specimens. Figures 24a and b (parallel tests) show the reduction of corrosion rates with time for three degrees of saturation with respect to calcium carbonate at a low velocity of 0.085 fps. The amount of calcium and alkalinity was 125 mg/l (as CaCO_3). The decrease in rate of corrosion occurred most rapidly for the water with a saturation index of +0.2 and least rapidly for the -0.8 saturation index water.

The specimens in -0.3 saturation index water leveled off at a higher final corrosion rate than either of the other two. It should be indicated that the specimens at this saturation index showed small dark reddish spots or growths surrounded by an overall whitish red deposit prior to the addition of chlorine, and continued to form tubercles. To a lesser extent, similar growths developed on the specimens in +0.2 saturation index water.

At point A, 56 mg/l sodium chloride (1.0 me/l) was added, and the saturation index was reduced to -0.1 and the pH to 7.5. The effect of sodium chloride is apparent. The addition of 5 mg/l silica at this point had no apparent effect on the corrosion rate, as can be seen in figure 24b.

Figures 25a and b provide similar data at 0.34 fps, but with combined chlorine present rather than free chlorine at point B. The more rapid reduction and the lower final corrosion rates testify to the effectiveness of a greater velocity to improve the diffusion rate of calcium as the inhibitor. Reducing the saturation index gave no change in the corrosion rate because of substantial protection previously developed.

With free chlorine added (figures 24a and b), it had been observed that round knobs of 3/16-inch diameter protruded as much as 1/8 inch. Similar tubercles, but smaller in size and number, were noted in the -0.3 saturation index environment when free chlorine was absent. After the specimens were cleaned, graphitization was observed where the tubercles had been, clearly indicating localized corrosion.

Parenthetically, the free- and combined-chlorine levels were maintained in these tests without substantial increase in chloride content by periodically replacing portions of the water with fresh water and adjusting the mineral composition.

Figures 25a and b show almost identical features. Figure 25b includes clear evidence of the effect of adding 56 mg/l sodium chloride to the -0.3 saturation specimens.

It is significant to note in both figures 24 and 25, the tuberculation was greater at the -0.3 saturation index than at either the higher or lower levels, and the corrosion rate continued at a high rate for a longer period of time. This is more striking at the low velocity in the figure 24 experiment than in figure 25.

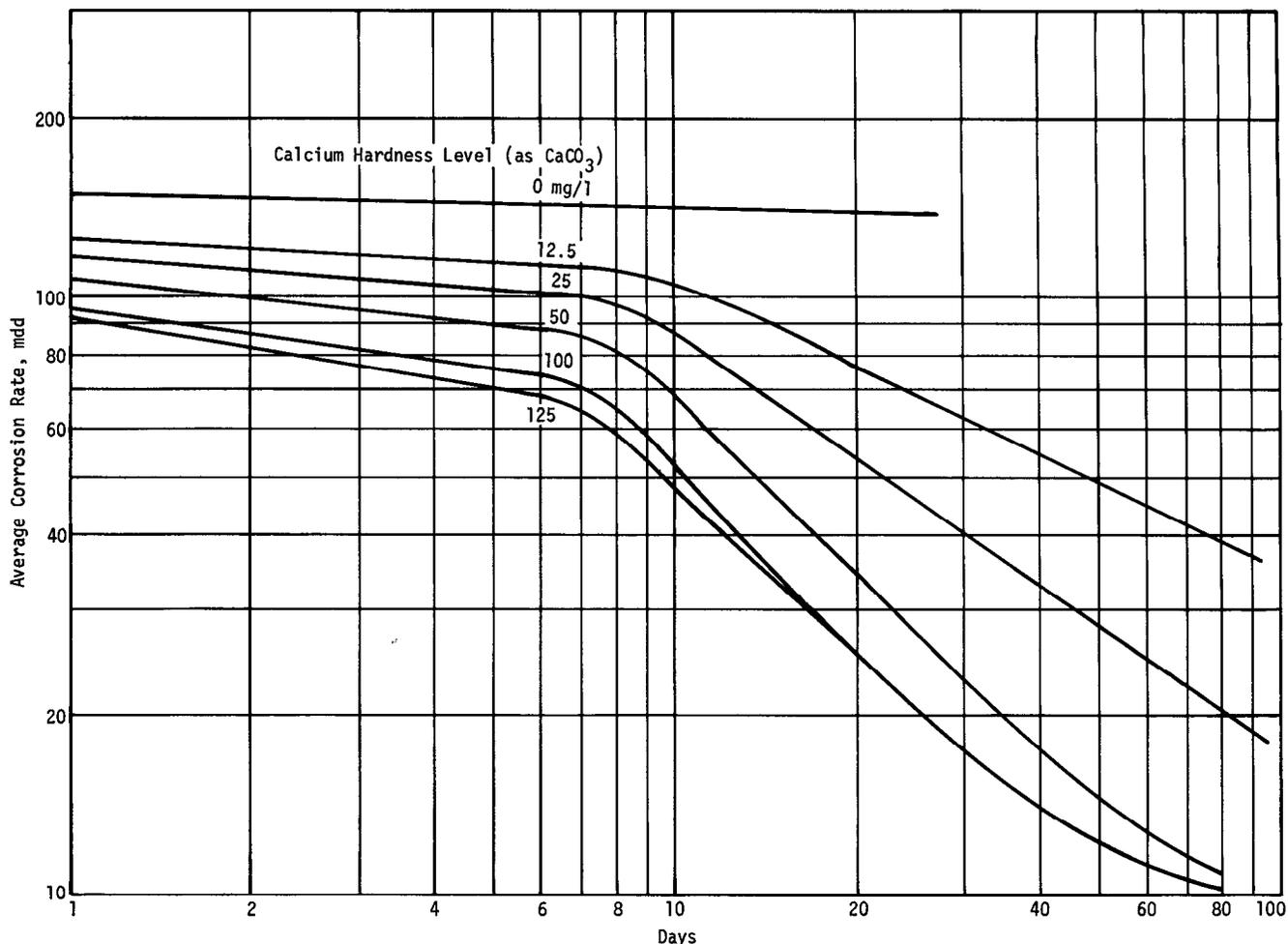


Figure 23. Summary of calcium effects on corrosion

Chloride to Alkalinity Ratio Effects. To consider further the relative influence of the calcium concentration, saturation index, chloride-alkalinity ratio, and chlorine, the results of four test conditions are indicated in figure 26.²⁷ All tests were made with a water velocity of 0.85 fps. Calcium concentration (as CaCO_3) was 31 mg/l; alkalinity (as CaCO_3) was 25 mg/l. The saturation index was -0.25 , and the pH (except as indicated) was 8.0. These machined cast iron specimens showed tuberculation in all cases, with or without chlorine or chloramine, and were similar in appearance to the -0.3 saturation index specimens as indicated in figures 24 and 25 with 125 mg/l calcium hardness.

Although the calcium concentration was lower than in figures 24 and 25, the rate of corrosion after 1 day was less than that when 125 mg/l calcium hardness was present. The rate of approach to equilibrium was lower and the final corrosion rate was higher.

The influence of the chloride-alkalinity ratio is shown in figure 26 by comparing the top and bottom curves; the intermediate ratio of 0.3 is also indicated by the two middle curves. The relative influence of free and combined

chlorine appears to be consistent with the observations in figures 24 and 25, but of only minor significance with this already more corrosive water.

Of particular significance is the rise in corrosion rate in one of the solutions at the 84th day, when the pH was permitted to drop to 6.7. On detailed examination of the data, it often appeared that an inadvertent drop in pH of 0.1 unit increased the corrosion rate by about 8 mdd.

From an applied standpoint, it is important to recognize that liquid chlorine is an acid, and converts alkalinity to carbon dioxide.¹⁶ This results in a reduced pH and consequently a reduction of the saturation index. Therefore a stable or protective water may be converted to one with corrosive tendencies. Just as alum (which is an acid when dissolved) requires neutralization by lime, caustic soda, or soda ash, so does liquid chlorine. For each mg/l chlorine added, 1.13 mg/l caustic soda is required for the neutralization. Of course, sodium hypochlorite can generally be substituted for liquid chlorine in small plants, with no need for neutralization.

pH Effects. One study was conducted to show the ef-

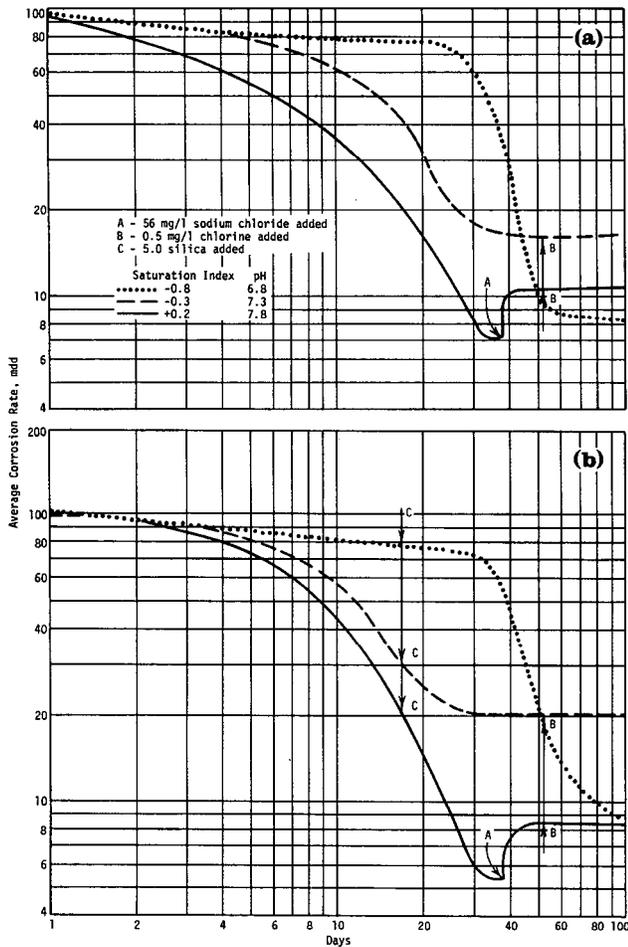


Figure 24. Tests made at 0.085 feet per second water velocity

fect of pH on the corrosion rates of cast iron at a flow rate of 0.1 fps for a zero hardness water having an alkalinity of 125 mg/l and a chlorine-alkalinity (Cl/alk) ratio of 0.2.²⁸ The results shown in figure 27 are generally similar to those obtained for steel specimens (see figure 19) exposed to similar water with no hardness and a chloride-alkalinity ratio of 0.15 at a velocity of 0.14 fps, in that the lowest average corrosion rate occurs at pH 7.0.

By comparison with the results for cast iron specimens illustrated in figure 26, this study with no calcium at pH 8.0 showed a corrosion rate of about 65 mdd at 100 days. Severe local pitting was noted adjacent to the paraffin coating over the edges.

Tuberculation on the machined cast iron surface increased with increasing pH in the range 7.5 to 9.0. This is in contrast to the general corrosion at pH 7 and lower. The thick corrosion products at pH 7 appear to be effectively resistant to the diffusion of dissolved oxygen, and thereby reduce the corrosion rate.

A similar study was made to determine the effect of the Cl/alk ratio on the corrosion of machined cast iron in waters with an alkalinity of 120 mg/l at calcium concentrations of

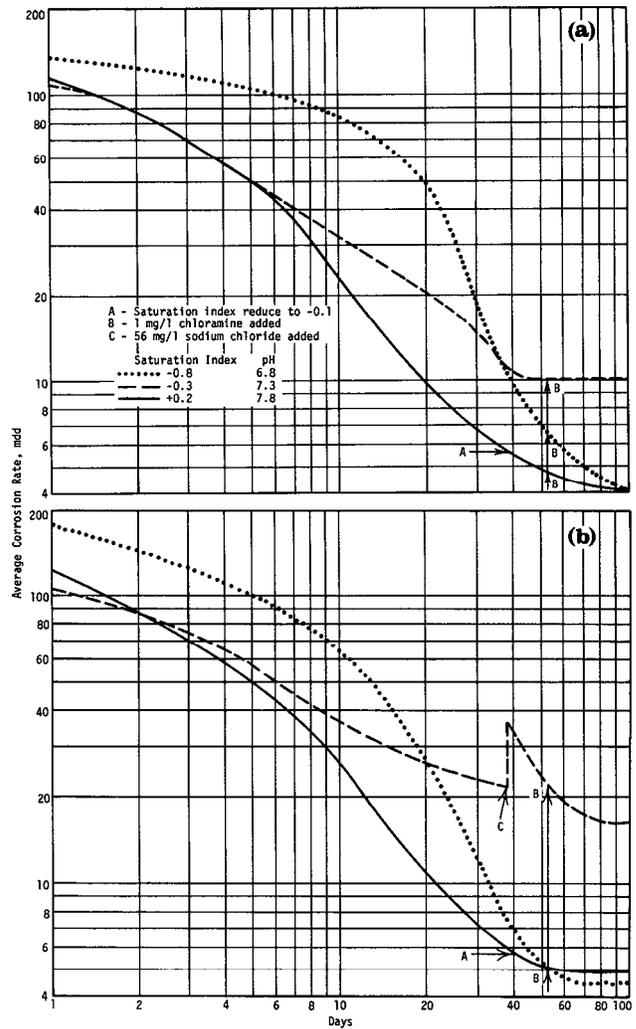


Figure 25. Tests made at 0.34 feet per second water velocity

30 and 85 mg/l.²⁸ In this study, the pH was regulated to maintain a zero saturation index and the velocity was 0.8 fps. The corrosion rates are shown in figure 28. It can be seen that the relationship of the Cl/alk ratio to the corro-

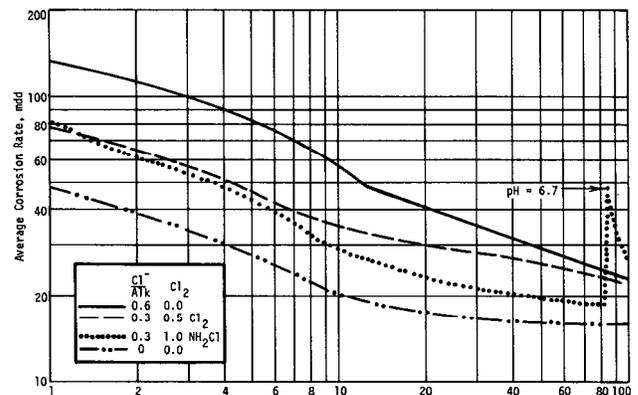


Figure 28. Effects of Cl/alk ratio and chlorine

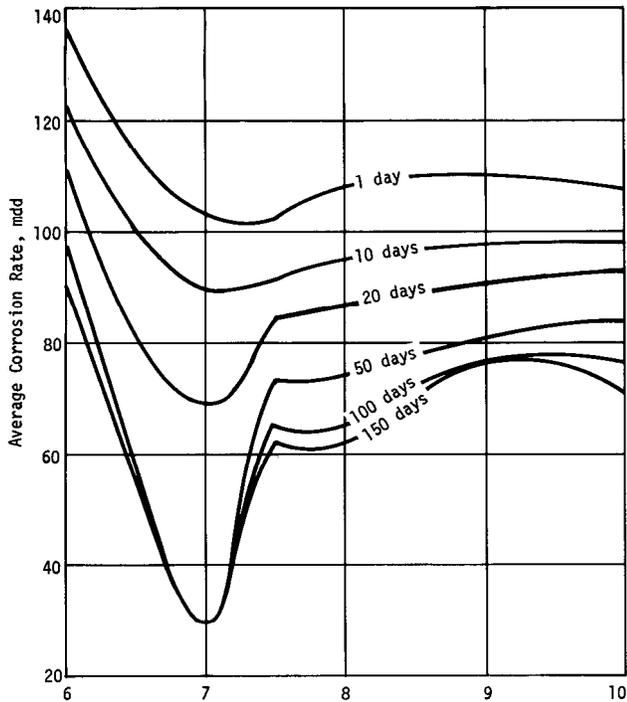


Figure 27. Relationship of corrosion rate to pH

sion rate is minimized within 30 days when the water is stabilized with respect to CaCO_3 . The beneficial effect of higher calcium hardness is shown even though the pH is lower.

In another series, tests²⁶ were designed to determine the relative influence of sulfate and chloride ions on tuberculation. No significant differences from the foregoing studies were noted with regard to corrosion rate or tuberculation in concentrations up to 30 mg/l sulfate and 3 to 25 mg/l chloride with water of an 85 mg/l calcium hardness, a 120 mg/l alkalinity, and a 0.29 $(\text{Cl} + \text{SO}_4)/\text{alkalinity}$ ratio at saturation indexes of -0.8, -0.3, and 0.0.

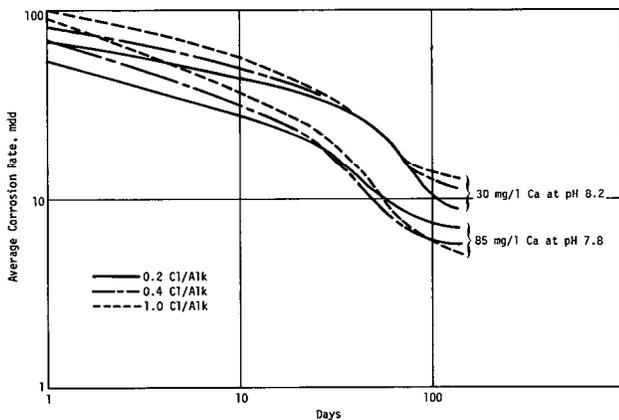


Figure 28. Decrease in average corrosion rate with time at 0 saturation index

When the pH was changed during the test from a 0.0 saturation index to a lower level, the corrosion rate increased. When the pH was changed from a negative saturation index to a 0.0 index, the corrosion rate decreased strikingly.

Relative Corrosion Rates. Sixty-seven experiments were conducted to determine the relative corrosion rates at room temperature of uncoated cast iron specimens (without natural scale protection) in oxygen-saturated, synthetic waters of different mineral composition which are not unusual for public water supplies.¹⁶ As in previous studies, the experiments were made at constant velocity with pH adjusted by the controlled addition of CO_2 . The instantaneous corrosion rate measurements were made by momentary polarization of the specimens twice a week. Tests were conducted long enough to establish a constant or equilibrium rate. This usually required an exposure of 3 to 4 months or more.

A summary of equilibrium rates is shown in figure 29. The velocity was 0.1 to 1.0 fps, and the temperature was 20°C. The initial rates were usually 100 to 150 mdd, and gradually approached the rates indicated in figure 29. The mineral variables were alkalinity, calcium, chloride, and sodium with the pH adjusted to the various levels indicated. The apparent general characteristic of these data is a maximum rate of corrosion at a particular pH level, with reduced rates at other pH levels (Ca and alk are expressed as CaCO_3).

The lower minima at about pH 6 to 7 represent evenly distributed general corrosion with a relatively thick layer of corrosion product which provides a protective barrier to corrosion. This product occasionally flakes off with a temporary increase in rate, which decreases as the thickness again increases. No tuberculation is evident. At somewhat higher pH levels the corrosion rate increases and tuberculation becomes apparent, particularly at the maximum corrosion rate and before the minimum rate at the upper pH level. In this range, cleaned specimens show areas of distinct graphitization similar to pitting attack under the points of tuberculation. The upper pH minima occur at or above the pH of saturation for calcium carbonate. At the upper pH minimum, the deposit is slightly rough but hard and either black or coated with a calcium deposit.

Similar characteristic maxima with respect to pH were observed by Uusitalo and Heinaneu²⁹ in Finland on *steel*, after the data had been replotted with respect to pH (figure 30).

Supplementing these studies, Stumm³⁰ conducted experiments to relate corrosion rates to the amount of calcium carbonate deposited on cast iron. An apparent conflict was evident by some experiments indicating a heavy deposit of calcium carbonate at pH 9.5 with an accompanying high corrosion rate, under conditions of high saturation index. Other experiments indicated very low corrosion rates with a very small deposition of calcium carbonate under

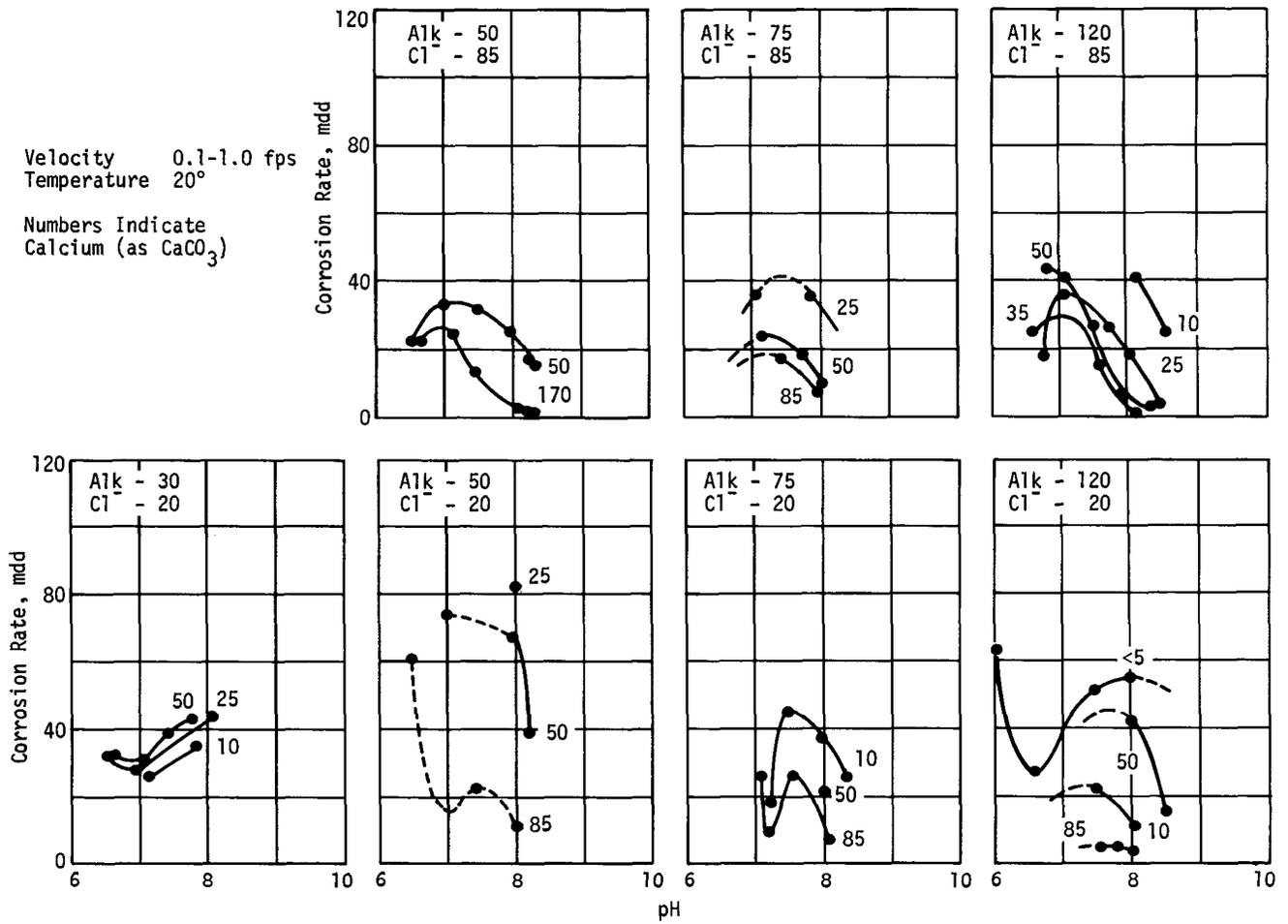


Figure 29. Summary of equilibrium rates

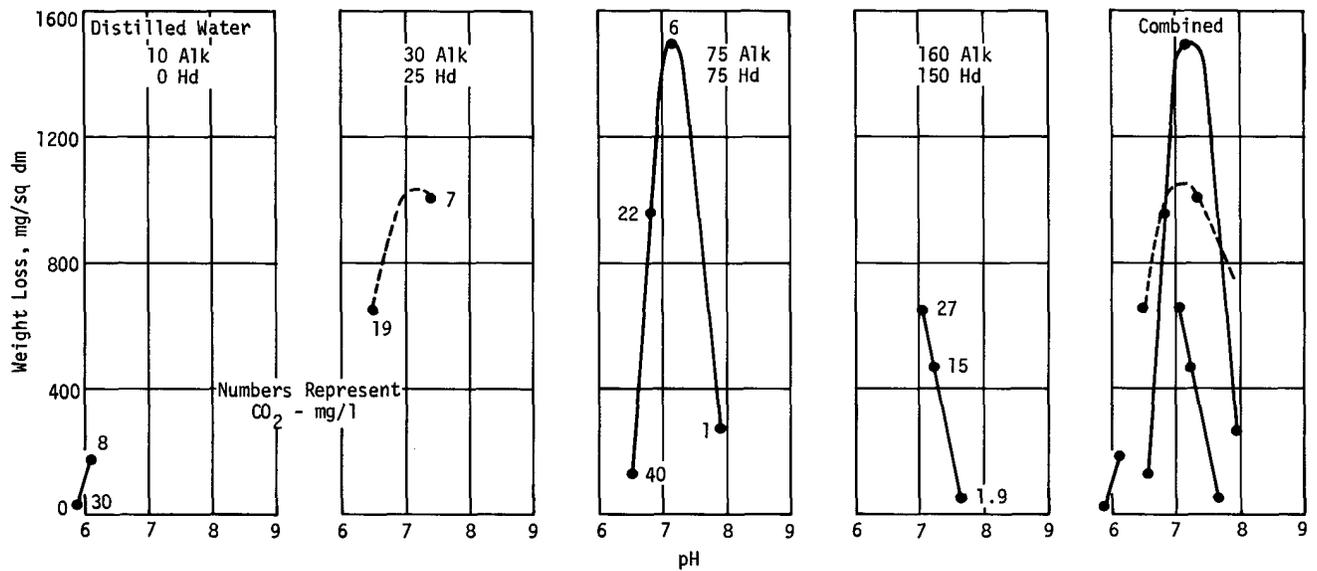


Figure 30. Corrosion of steel specimens

conditions of a slightly negative saturation index. This was attributed to the pH effect.

The high pH water had a calcium content of 55 mg/l (as CaCO₃) and an alkalinity of 50 mg/l (as CaCO₃) which provided only a minimum buffer capacity at pH 8.5. The low pH water (pH 7.1) had calcium contents of 190 and 250 mg/l and an alkalinity of 250 mg/l with about a 50-fold greater buffer capacity.

It was recognized that calcium carbonate is basically a cathodic inhibitor and deposits at the cathodic areas of the surface. Microscopic examination of the specimens in the high pH water showed the protected cathode areas to be quite large, and the anodic areas also quite large, as distinguished from observations on the specimens in the low pH waters where the anodic areas were numerous and very small, as in general corrosion. This latter condition permitted clogging of these small anodic areas with the corrosion product and calcium carbonate, as indicated by significant ennoblement of the corrosion potential after 20 days of exposure, whereas the high pH water was unable to block the large active anodic areas, and little ennoblement occurred during the exposure.

Thus, the combination of high alkalinity and calcium with the inherent low pH, can prevent corrosion more easily than low alkalinity and calcium, even with a high pH and a positive saturation index.

Summary

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. The basic corrosion reaction at the cathodic points is conducive to the formation of calcium carbonate at the point

of corrosion even though the water environment is below saturation with respect to calcium carbonate. The rate at which such deposition may take place is increasingly decreased by higher concentrations of calcium and/or alkalinity. The rate is further improved by pH adjustment up to or above the saturation pH for calcium carbonate, and under the higher pH levels the rate is also increasingly improved by higher velocities.

The finding that tubercles form under conditions below, but near, complete protection is consistent with the well-known action of all cathodic 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 graphitization under tubercles on the specimens. 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 (see figures 24 and 25) 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 0.5 inch.²⁷ There were no pits under this deposit and it served as an effective barrier to the diffusion of oxygen and other corrosive agents.²⁶

The finding that chloride accelerates corrosion of cast iron is consistent with the observations on steel specimens.

CORROSION PROBLEMS IN HOUSEHOLD AND INSTITUTIONAL FACILITIES

In contrast to central public water supply distribution systems, private homes, apartments, business and commercial buildings, and institutional buildings and grounds use water for many purposes, with multiple accompanying problems. Experience has shown that materials of construction are basic to corrosion control, and a variety of materials are available for selection as well as coatings for protection. Differences in water supply qualities may be more or less aggressive to different metals and may dictate the primary choice. A more expensive selection of piping and appurtenances can avoid costly chemical treatment. Minor modifications in water quality in some instances may be able to correct a severe problem. However, water treatment alone cannot be expected to control corrosion under adverse con-

ditions of poor choice of construction materials for specific uses, of inadequate design, and of excessive temperatures.

Materials of Construction

Although materials of construction are necessarily selected on the basis of their physical and mechanical properties, corrosion resistance is an important consideration for maintenance and the useful life of the installation. Lack of experience and knowledge to anticipate problems of leaks and failures from corrosion, or the contamination of the water with toxic metals or esthetically unacceptable products of corrosion, can be costly.

Cost considerations for the selection of materials should

always include cost of maintenance, ease of fabrication and repair, the life expectancy of the installation, and water treatment requirements if necessary.

Steel, iron, galvanized steel, copper, and aluminum are readily available at reasonable cost. Brasses are generally used for valves and fittings, and stainless steels are available for special needs if necessary. Plastic pipe and fittings are competitive and useful, where the high coefficient of expansion with temperature is not prohibitive.

Mild Steel. The process of manufacturing and the composition do not significantly affect the corrosion rate of mild steel in domestic waters. Copper bearing steel with proven effectiveness in air is no better in water than mild steel without copper. The presence of mill scale on the surface accelerates pitting by galvanic action.

Dissolved minerals with increasing chloride and sulfate concentrations increase the conductivity of water and may thereby increase the corrosion rate. With increasing proportions of alkalinity in the form of bicarbonate to the chloride and sulfate, and increasing proportions of calcium hardness to sodium and magnesium, the corrosion rate can be inhibited (see page 7 for stability). For any given water with insufficient calcium hardness and alkalinity, the corrosion rate is proportional to the concentration of dissolved oxygen and, generally, to the rate of flow. At low flow rates where the corrosion product (rust) remains on the surface, the rate of diffusion of oxygen to the surface is hindered and the corrosion rate is reduced until the deposit flakes off.

Elevated steel tanks should be painted periodically in accordance with AWWA Standards (D102-64), and should have properly installed and controlled cathodic protection systems.

Zinc and Galvanized Steel. Zinc like aluminum and lead is an amphoteric metal and corrodes in alkaline as well as acid solutions. In the absence of carbon dioxide or the carbonate species, it has minimum solubility in a relatively narrow pH range near 9.3.³¹ In distilled water corrosion increases with rise in temperature from 120°F to a maximum at about 160°F where the corrosion product is not adherent and then decreases above 160 to 212°F as the solubility of oxygen decreases.³²

In distilled water at 85°F, over a range of controlled pH levels from 2.6 to 14.4 with HCl and NaOH, the corrosion rate of zinc was less than 0.05 inches per year between pH 6 and 13.³³ Increasingly rapid corrosion was recorded as the pH deviated below 6 and above 13.

In natural waters corrosion of zinc is dependent upon the pH, alkalinity, and type of dissolved minerals. With adequate carbonate hardness (alkalinity and calcium), protection by basic zinc carbonate is often effective at or near the pH of saturation for calcium carbonate.

Galvanized steel relies on a zinc coating for protection of the steel from corrosion. The zinc protects the steel by

excluding water contact with the steel and also by galvanic protection, where the anodic zinc corrodes more easily than cathodic steel. Zinc is sacrificed for the protection of the steel at holidays and other exposures. If on the other hand the zinc corrosion products completely protect the zinc, its sacrificial property is negligible and pitting at the steel exposure can take place, unless the steel was galvanically protected by calcium carbonate at early exposure.

In waters containing calcium bicarbonate, anodic dissolution of zinc develops a film of basic zinc carbonate at anodic areas and a film of calcium carbonate at exposed iron areas. Such deposits may be hindered by relatively high concentrations of sulfates and chlorides, and by insufficient concentrations of calcium and alkalinity. Large areas of exposed steel at joints and threads are particularly affected by these conditions. Traces (0.1 mg/l) of soluble copper can also be detrimental to zinc coatings, and galvanic corrosion of zinc is accelerated by contact with copper, or copper bearing metals.

Aluminum. The corrosion resistance of aluminum is due to the protection developed by an inert oxide film. This film can be destroyed by acidic conditions (pH ≤ 7). The presence of copper, and high chloride concentrations, can generate local corrosion in the form of pitting. Aluminum should never be used in systems involving copper bearing metals.

Copper. The corrosion resistance of copper is usually due to an oxide film, and the various grades of copper differ little in resistance to corrosion. The loss of resistance by destruction of the oxide film does not necessarily lead to severe attack as with aluminum. Copper is subject to severe impingement attack at high rates of flow (>4 fps) particularly with soft waters with appreciable bicarbonate alkalinity and carbon dioxide. The presence of dissolved oxygen in such waters has also been implicated. The impingement can be particularly severe with high turbulence at elbows and constrictions to flow. The impingement takes the form of pits, usually in a 'horseshoe' shape.

General corrosion of copper at low velocities is enhanced by insufficient calcium hardness and alkalinity, accompanied by chloride and sulfate. Dissolved copper causes blue to green stains on porcelain ware. (Copper should never be used with low pH carbonated water.) Hot water temperatures enhance the rate of corrosion by such waters. Pitting corrosion can take place with hard waters where debris or particles of cement or sand adheres to the surface and prevents access of dissolved oxygen to the metal surface.

Copper Alloys. There are a number of copper alloys with zinc and nickel. The more common copper-zinc alloys for household systems are yellow brass 67-33 copper-zinc, and red brass 85-15 copper-zinc. The flexibility of copper pipe is sacrificed for strength, and often for better corrosion resistance. The yellow brass is subject to dezincification in soft waters with appreciable carbon dioxide, and

with water of high pH (>9.0 to 9.6), particularly with high chloride and/or at high temperatures. Red brass is preferable for piping and valves with such waters.

The copper-nickel alloys appear to be superior for difficult conditions. The 90-10 and the 70-30 copper-nickel alloys generally provide good service in hot water heater temperatures. If 1 percent iron is included in the product, corrosion resistance to high velocities is improved.

Stainless Steel Alloys. There are a great number of types of stainless steels with different physical and mechanical properties, depending upon heat treatment and annealability. The properties of these alloys often dictate choice and often with no attention to corrosion resistance behavior. However, under certain conditions, their resistance to corrosion is far from good. Other selections are made with great care for corrosion behavior for acids or sea water exposure.

Chromium-iron alloys at 3 percent Cr show some improved corrosive resistance over steel, but for true 'stainless' properties at least 12 percent Cr is required. However, even at higher chromium percentages, there is still a risk with high chloride waters. The 11 percent chromium-iron alloy tubing (Type 409) represents an example of poor corrosion resistance at the seam, particularly in waters with high chloride concentrations.

The corrosion resistance of true stainless steel is due to a very thin protective oxide on the metal surface. Maintenance of this film is dependent upon oxygen. Lack of oxygen can develop in crevices and under debris, with resulting localized corrosion. For this reason surfaces should be maintained in a scrupulously clean condition. Type 304 (18 percent Cr, 8 percent Ni) is a general all purpose stainless steel that is used quite frequently in water treatment plants and for well screens. Where pitting attack may be experienced or anticipated, Type 316 (18 percent Cr, 8 percent Ni, 2 to 3 percent Mo) offers greater resistance. The presence of chloride causes susceptibility to stress-corrosion cracking. Related factors in stress-corrosion cracking are temperature, concentration of chloride, and degree of stress. For this reason stainless tubing has yet to be accepted for household waters, although it is extensively used for food preparation, cutlery, table tops, sinks, and other household facilities.

For environments of excessive temperature, chloride, and stress, where stress-corrosion cracking may be anticipated, there are other more highly alloyed grades of stainless steel available.

Galvanic effects with copper or copper alloys are negligible when coupled to 18-8 stainless steel.

Water Quality Considerations

Because of the limitation of treatments for household distribution systems for drinking water quality, the *first line*

of defense in corrosion control must be the selection of materials. Acceptable piping may generally be red brass or bronze, yellow brass, copper, 90-10 copper-nickel, or galvanized iron. The selection should be based on the mineral quality of the water and the need for and selection of treatment alternatives. The following assessments and recommendations can be made from experiences in state institutions in Illinois.

Cold Water Corrosion and Treatment

Surface Waters. Water from streams and lakes contain dissolved oxygen, approaching saturation concentrations. Such waters are normally clarified, filtered, and chlorinated, and frequently (too often) are not adequately adjusted to the proper pH for stability with respect to scale and corrosion control.

For waters of high alkalinity and hardness, greater than 150 mg/l, copper service lines may be preferred. However, galvanized steel may prove satisfactory, particularly if the pH is raised to slightly above the stability pH of saturation. If the chloride and sulfate level exceeds 150 mg/l, supplementary treatment with 8 mg/l liquid sodium silicate (as SiO_2) can be beneficial.

For low alkalinity and hardness surface waters, less than 150 mg/l (as CaCO_3), copper is preferred. Galvanized iron may be satisfactory if the pH is adjusted to the pH of calcium carbonate saturation, or higher. If the chloride and sulfate level exceeds 80 mg/l, sodium silicate formulation can be beneficial.

A 2-year exposure of various pipe materials to waters of different qualities at 19 cities in the United States and Canada³⁴ showed no corrosion of aluminum piping in lime softened water at 7 cities. The greatest hazard with aluminum, is the presence of copper or a low pH.

Groundwater. For groundwater with high hardness and alkalinity (>150 mg/l), with characteristically little or no dissolved oxygen, and with a combined chloride and sulfate concentration of less than 150 mg/l, galvanized iron or copper piping is satisfactory. For higher chloride and sulfate levels, copper is the preferred material.

If such water is softened by ion-exchange, hard water should be blended with the softened water to provide a hardness of 60 to 100 mg/l, and galvanized iron can be satisfactory with low chloride and sulfate, but copper is preferred with higher levels. Supplementary treatment with sodium silicate (8 mg/l as SiO_2) at pH 8.0 to 8.4 can be beneficial to copper as well as galvanized iron.

Hot Water Corrosion and Treatment

Corrosion of galvanized piping is more severe above 140°F. Maintenance of hot water temperatures below a maximum of 140°F is an important factor in controlling

corrosion. If higher temperatures are required for dishwashing or laundry purposes, such systems should be designed for periodic replacement of common piping materials, or should be constructed of more corrosion resistant materials such as red brass, 90-10 copper-nickel, stainless steel, etc.

In hot water (140°F) piping, 'zero softened' water causes very serious corrosion of galvanized steel piping. Blending with hard water to provide 60 to 100 mg/l hardness has generally provided successful corrosion inhibition. With highly mineralized water ($\text{Cl}^- + \text{SO}_4^{--} > 300$ mg/l), liquid sodium silicate accompanied by a pH increase with caustic soda from pH 7.9 to 8.4 is beneficial, if the alkalinity exceeds 150 mg/l.

Compatible materials should be installed in the same system; for example, cement-lined hot water heaters should be installed with galvanized piping. Copper steam coils or dip tubes should never be used with galvanized hot water heaters.

Hot water systems employing copper tubing should be designed for flow rates of less than 4 fps.

In rehabilitating old buildings and adding buildings to an institution already served by a central circulating hot water system with compatible materials, the same type of piping should be installed in the new buildings as in the old.

Sodium polyphosphate, which is ineffective as a corrosion inhibitor under low velocity conditions, is also not considered a generally effective inhibitor under other velocity conditions encountered in water distribution systems unless concentrations exceed 15 to 25 mg/l.

Treatment Evaluations. In an effort to evaluate materials for institutional and domestic hot water distribution systems for a number of different types of water qualities, and to investigate a variety of chemical treatment methods, controlled laboratory and field studies were made by the State Water Survey at several Illinois state institutions for the Department of the Air Force.^{35,36,37} The selections were based on the quality of water, the feasibility for altering the quality for controlled experiments, and space requirements for the controlled studies.

Five types of water were included in the study with the use of steel, copper, 90-10 copper-nickel, and galvanized steel. In addition to a control exposure in the unaltered water, the following treatments were tested: liquid sodium silicate with or without pH adjustment, zinc silicate* with sulfamic acid, zinc polyphosphate,** and zinc monobasic phosphate*** with sulfamic acid.

* Zinc silicate formulation
8 mg/l SiO_2 (as liquid silicate) + 3 mg/l Zn^{++}
(as $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$) + 1 mg/l sulfamic acid
(as $\text{H}_2\text{NH}_2\text{SO}_3$)

** Zinc polyphosphate formulation
U. S. Patented formula by Calgon, Inc.
Zinc polyphosphate, composed of:

Phosphorus pentoxide (P_2O_5)	56.5%
Zinc oxide (ZnO)	11.0%
Sodium oxide (Na_2O)	32.5%

*** Zinc monobasic phosphate formulation
U. S. Patent 3669616 formula by Virginia Chemicals, Inc.

Zinc sulfate ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$)	55.3%
Sulfamic acid ($\text{H}_2\text{NH}_2\text{SO}_3$)	20.0%
Sodium monobasic phosphate (NaH_2PO_4)	24.7%

For each of five types of water with no treatment, 90-10 copper-nickel was found to be preferable to copper, at 140 and 180°F, and both were much preferred to galvanized steel and to steel. For steel pipe, no treatment used was found to be effective.

- 1) Waters of low hardness (20 mg/l) and alkalinity (20 mg/l) with 75 mg/l total dissolved minerals, at pH 7.0:
 - a) For improved resistance for both copper and 90-10 copper-nickel, liquid sodium silicate (8 mg/l SiO_2), or 5 mg/l zinc polyphosphate formulation, or 6 mg/l of zinc monobasic phosphate formulation, seemed preferable to the zinc silicate formulation at 140 and 180°F.
 - b) For galvanized steel, liquid sodium silicate was not evaluated at pH 7, but at pH 8.4 (8.2 mg/l SiO_2) it was reasonably effective at 140 and 180°F.
- 2) Waters of very low hardness (6 mg/l) and a high alkalinity (340 mg/l) with high chloride plus sulfate (200 mg/l):
 - a) For copper and 90-10 copper-nickel, 5 mg/l zinc polyphosphate formulation at pH 7.0 was satisfactory at 140 and 180°F.
 - b) For galvanized steel, liquid sodium silicate (10 to 20 mg/l SiO_2) improved the corrosion resistance at pH 8.0 to 8.3.
- 3) Waters of 65 to 90 mg/l hardness, 350 mg/l alkalinity, and 180 mg/l chloride plus sulfate at pH 7.8 to 8.1:
 - a) For copper and 90-10 copper-nickel, either 6 mg/l zinc monobasic phosphate formulation or zinc silicate formulation (8 mg/l SiO_2), except at high velocity for copper, provided protection at 140°F but the 6 mg/l zinc monobasic phosphate appeared to be preferable at 180°F.
 - b) For galvanized steel, liquid sodium silicate (11 to 22 mg/l SiO_2) at pH 8.1 was effective, and zinc silicate formulation (8 mg/l SiO_2) at pH 7.8 appeared to be generally somewhat better than 5.6 mg/l zinc monobasic phosphate formulation and liquid sodium silicate (4 mg/l SiO_2) at 140 and 180°F.
- 4) Waters of 150 mg/l hardness, 120 mg/l alkalinity, and 300 mg/l chloride plus sulfate at pH 6.8:
 - a) For copper and 90-10 copper-nickel, with pH adjustment to 8.3, improved corrosion resistance at

140°F was noted with liquid silicate (8 mg/l SiO₂), or zinc silicate formulation (8 mg/l SiO₂) at 180°F.

- b) For galvanized steel, with pH adjustment to 7.8, liquid sodium silicate (10 mg/l SiO₂) provided greater corrosion resistance at 140°F than that observed at pH 8.3 with 7 mg/l as SiO₂ or zinc silicate formulation (8 mg/l SiO₂).
- 5) Waters of 70 to 80 mg/l hardness, 260 mg/l alkalinity, and 600 mg/l chloride and sulfate:
 - a) For copper, liquid silicate (11 to 22 mg/l SiO₂), and for copper and 90-10 copper-nickel, zinc silicate formulation (8 mg/l SiO₂) at pH 8.2 appeared to have a slight corrosion resistance advantage over the phosphate formulations at 140 and 180°F.
 - b) For galvanized steel, liquid sodium silicate (11 to 22 mg/l SiO₂) at pH 8.1 was preferable at 140 and 180°F to 5 mg/l zinc polyphosphate formulation, and 6 mg/l zinc monobasic phosphate formulation at pH 7.7 was preferable to zinc polyphosphate formulation at 180°F.

The assessments on treatment for 120-day periods for galvanized iron were made on the basis of change in weight between the original weight of the test specimens, and the weight recorded after removal of all loose scale and corrosion products. It was not possible to remove the tight scale without removing some of the remaining zinc. The weight loss (or weight gain, indicated as a negative value) therefore included the actual corrosion loss plus the hard tight scale from the corrosion product and the treatment.

Although basically five types of treatment were used for the entire study, in no case were all tested for the five types of waters, and in no case were the levels of treatment varied to suggest optimum dosage. These observations therefore are suggestive for each type or for all types of waters. For any one type, the variables of original quality are limited

until a more thorough study can be conducted to better evaluate the types of treatment.

Validation of Performance

For evaluating the resistance of metal piping to corrosion and/or the effectiveness of treatment, in-line testing can be a very useful tool to determine the effect of water quality and, if necessary, the treatment applied for protection. Water Survey personnel have developed a test specimen holder for removable pipe inserts, insulated from a metal cylinder by a PVC³⁸ sleeve. The cylinder can be installed in the pipe line with PVC spacers. The internal surface is not altered, and the dimensions are designed to prevent any distortion of stream line flow. A specimen holder for 1-inch inside diameter pipe is illustrated in figures 31 and 32. This corrosion tester, developed by the State Water Survey, has been adopted as an ASTM-D2688 Standard.

The inserts are prepared by reducing the external diameter to 1.125 inches in a lathe to permit an accurate weight measurement before and after exposure. The original weight of the insert is approximately 100 grams. The external surface and the ends of the insert are painted with a coat of epoxy primer to avoid undue corrosion of the exterior and the end edges. After exposure, the paint is removed with an epoxy stripper and the specimen properly cleaned from scale and/or corrosion products before drying and weighing again to determine the weight loss.

The minimum time of exposure is usually about 60 days for the downstream insert, and 180 days for the upstream specimen. Results may be expressed as milligrams per square decimeter per day or in inches per year (see page 20). After weighing, the specimen is sawed lengthwise and the corrosion is evaluated by noting the number and depth of pits.

RESEARCH NEEDS

There is a great lack of application of research on many aspects of preventive maintenance related to corrosion by water. At the same time, research and experience have already pointed to solutions of corrosion problems. Some solutions lie in metallurgy and fabrication, others in effective coatings, and others in chemical treatment. Applications of research, which generally lag many years behind the research findings, sometimes have limitations not easily recognized. Sometimes the cost and effort are judged not to be worthwhile. Sometimes the corrosion is out of view and not readily available for inspection. But where serious corrosion is recognized and there is knowledge on prevention, failure to use the best technology is inexcusable.

It is rare that any study does not require more information for confirmation, better data for refinement, or more exact definition of the limitations. It is also rare to find complete solutions. Even if fundamental principles are well known and documented, research is often required to apply the principles in the most effective way. Some of the research needs related to corrosion are in the following areas.

No common metal or alloy is universally acceptable for all potable water for public water supplies and domestic uses under various conditions. Copper tubing has become the predominant metal for plumbing, where applicable, but for many waters, it has experienced notable failures. Also, copper is becoming very expensive and its supply short.

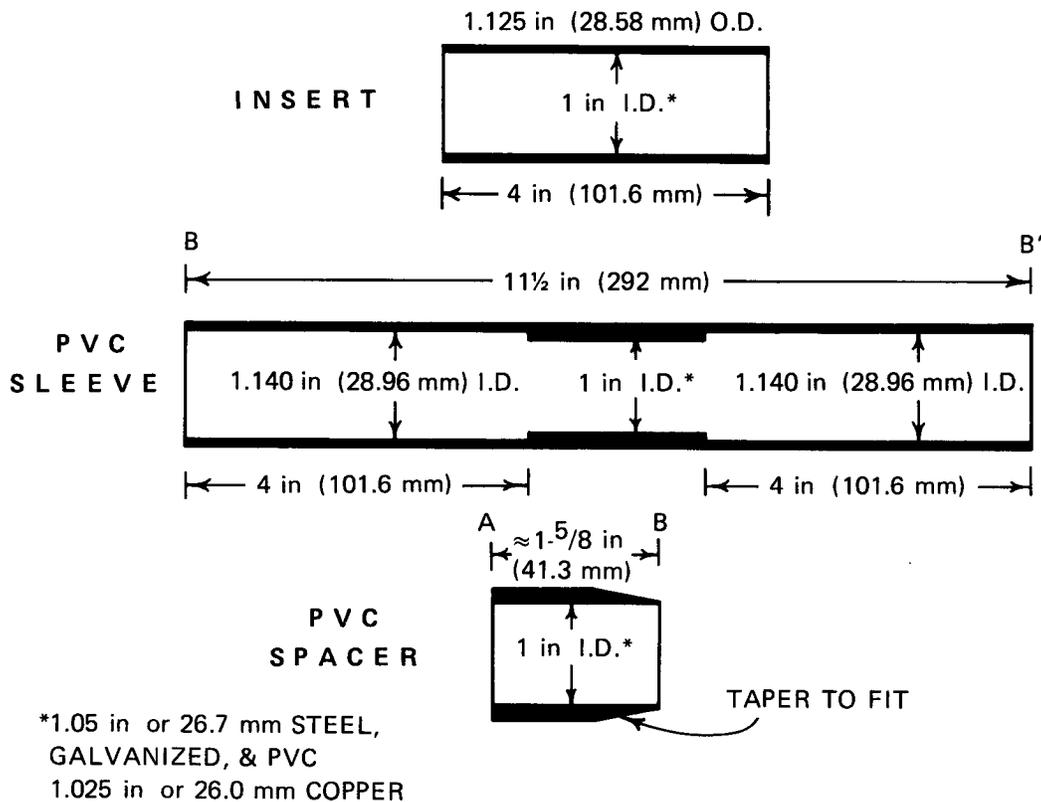


Figure 31. Insert, sleeve, and spacer of State Water Survey corrosion tester

As an alternate, thin wall stainless steel for household use shows some promise, but fabrication problems have yet to be overcome. Also, work being done on protecting galvanized pipe with a tightly adherent alumina-silicate coating should be continued.

The performance of each metal and alloy is often different for waters of different water quality characteristics. There is a great need to clearly define the limitations of each for the various types of water under different temperature and velocity conditions. This information is needed to determine the best combination of metals and the necessary treatment.

A companion need is to determine more clearly the effectiveness of various corrosion inhibitors for different metals, alloys, and coatings – again for the various water quality characteristics. Limitations on inhibitor composition and concentration for potable waters, related to toxicity and cost, require the best combination of materials of construction, and if necessary the best inhibitor.

Increasing chloride concentrations are evident in many water supplies. The source is usually from direct discharge to streams and lakes from road salt, waste treatment effluents, industrial wastes, and on occasion salt mining. Be-

cause chloride can increase corrosion rates, it would be desirable to define more precisely the rates of increase of corrosion in various waters under conditions of higher chloride.

Because drinking water standards limit the concentration of lead (0.05 mg/l) and cadmium (0.01 mg/l) which is an impurity in zinc, and because lead and zinc are exposed to potable water in plumbing and appurtenances, it is important to know what concentrations are present at the household tap resulting from corrosion. Copper imparts some taste to water at 1 to 5 mg/l and stains plumbing fixtures. Anodic stripping analytical techniques can detect very low concentrations and can be a useful tool to evaluate these corrosion products of health and esthetic significance. A survey of water quality characteristics in public supplies related to concentrations of these metals as corrosion products should have a high priority.

Corrosion often progresses undetected because it is out of sight in distribution systems and household piping. There is a need to evaluate and improve upon the polarization technique for internal instantaneous corrosion rate measurement. This is particularly important for evaluating the effectiveness and control of treatment with inhibitors.

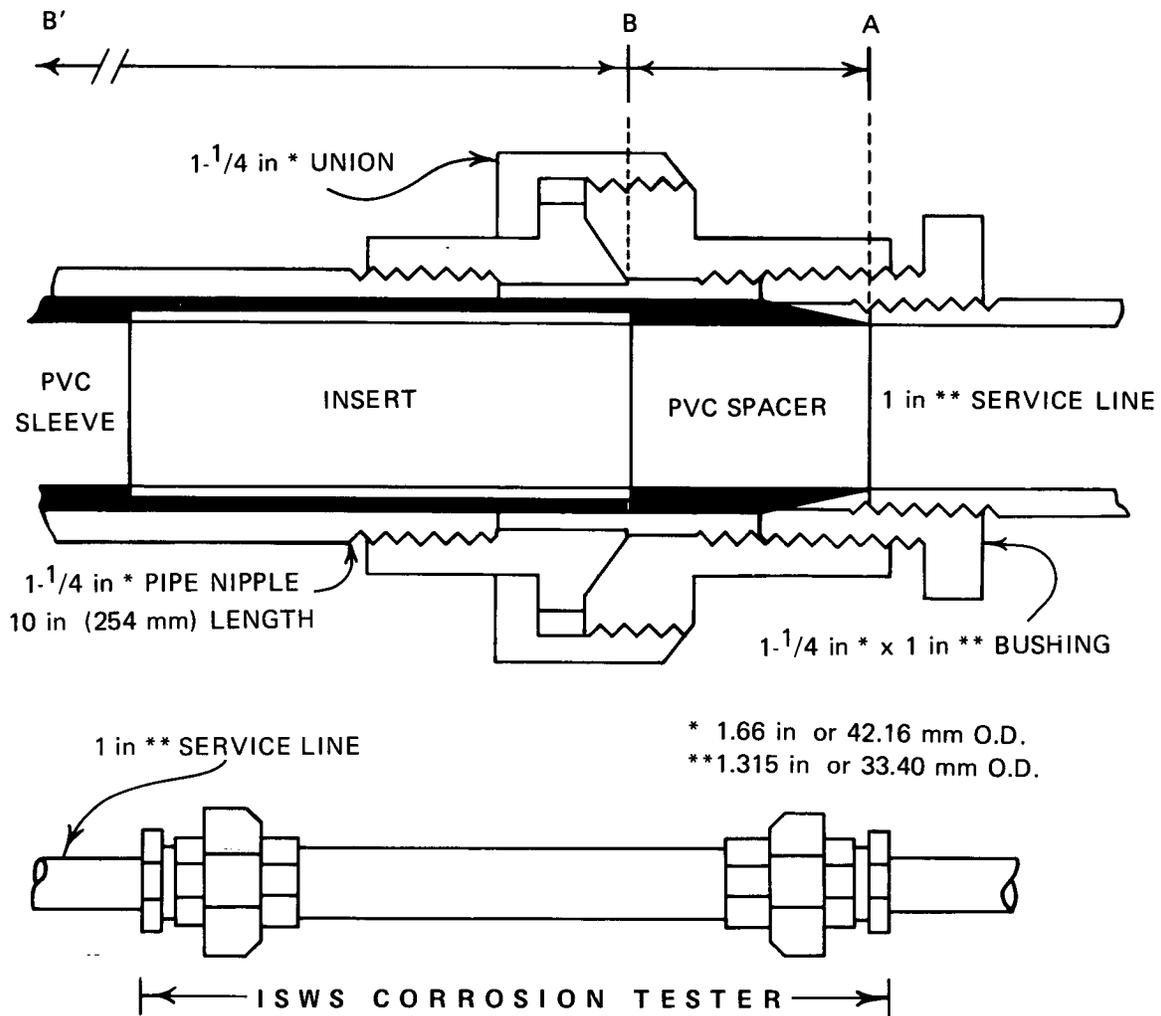


Figure 32. Cross section of insert, spacer, and union, and assembled State Water Survey corrosion tester

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Appendix A. Corrosion in Water Wells and Pumps

Corrosion in water wells is particularly difficult to assess for both cause and degree, because there is no possibility for actual observation and measurement while in service. Pumps in deep wells at deep settings are of particular concern because of the cost and time for removal and replacement. Also, the purchase cost of column pipe, shaft, and shaft tube is often greater than the cost of the turbine itself. Unless a regular schedule for removing the pump to assess damage is practiced, the pump may fail during a critical pumping period. If the scheduled interval is too short, and no damage is noted, the cost of removal of the pump and its return to the well can be an excessive burden on the maintenance budget.

A variety of metals can be used to construct vertical turbine pumps. Bronze, cast iron, steel, and stainless steel are often used together for an acceptable period of useful life with no serious problems at all. However, copper bearing metals with a metallic connection in the water to steel or cast iron always provides a potential for galvanic action where the copper bearing alloy is cathodic to the anodic ferrous metal. Galvanic action is accelerated by highly mineralized water, and by close physical proximity of dissimilar metals.

Within the turbine pump, the shaft to which the bronze impellers are attached is usually stainless steel. These two alloys are relatively close in the galvanic series (see table 1, page 2) and there is seldom any significant galvanic action except with very highly mineralized water. If the shaft were made of carbon steel, severe corrosion of the exposed shaft could take place between the bronze bearing and the bronze impeller.

The bowls surrounding the impellers and the shaft are usually made of cast iron, and often have an acceptable service life with bronze impellers because the bowls are not adjacent to the shaft and the impellers. However, the inside of the bowls is subject to corrosion particularly when exposed to waters with an appreciable proportion of non-carbonate minerals or waters containing high concentrations of carbon dioxide. The high turbulent velocities generated by the impellers prevent adherence of protective corrosion products. Severe problems with cast iron bowls are overcome by substituting all bronze bowls.

If the bowls are cast iron, current can flow from the cast iron to impellers. Each stage of the pump is designed to prevent back flow to the underside of the impeller. This is accomplished by providing a skirt at the underside of the impellers leaving very little clearance between the bronze skirt and the surrounding cast iron. This is the 'heart' of the pump where slippage cannot be permitted without impairing the efficiency. Close clearance here provides minimum resistance to current flow, and therefore the greatest corrosion rate of the cast iron. In many cases manufacturers

circumvent this by inserting a permanent or replaceable bronze wear ring attached to the cast iron surrounding the impeller skirt, thereby eliminating accelerated corrosion at this vital point by transferring the current to less vital areas of the bowls and reducing the concentrated attack.

Some attempts have been made to construct the turbine with all ferrous metals rather than dissimilar metals – steel shaft, cast iron bowls, and cast iron impellers. None of these have been successful.

Below the bowls there is often a tailpipe which may be 1 to 10 feet long in order to guide the water to the bowls. In some installations a slotted strainer is attached to the bottom of the tailpipe. The need for a long tailpipe is unclear, and the need for a strainer is even less clear since both offer a restriction to flow and tend to release carbon dioxide and other gases naturally in the water to escape and cause corrosion and other difficulties.

Even with the best of design of the bowl sections, other corrosion problems may take place in the column pipe assembly to transport the water to the surface. The assembly may include an oil lubricated shaft with bearings and an oil enclosure tube, or a water lubricated shaft with bronze bearing retainers inserted at intervals between column pipe sections. The oil tube is similarly supported by 'spiders' at intervals.

For water lubricated pumps, the bearing for the shaft is usually a type of synthetic rubber, and the bearing retainer is brass or bronze. With a stainless steel shaft few if any problems occur, but carbon steel shafts have been observed to corrode immediately opposite the upper and lower ends of the retainer for the bearing.

Some installations apparently permit a series of galvanic cells within the column pipe assembly and the adjoining turbine unit which enhance each other and increase the rate of corrosion. This is similar to short circuiting the open terminals of two batteries which have been connected in series. In figure A, a self-imposed current can flow from the cast iron bowls to the impellers and be conducted up the shaft to flow to the bearing retainers or the bearing (if the water is permitted to enter the lower end of the oil enclosure tube), and return to the bowls by way of conduction through the column pipe or the oil enclosure tube.

For either type of lubrication, steel column pipes have been observed many times to corrode more or less severely within about 2 feet above the discharge bowl of the turbine unit. For oil lubricated pumps similar action takes place at the outside of the oil tube. To a progressively lesser extent this action on the column pipe and on the oil tube occurs just above the bearing retainer and the spiders. Each of these points of attack is located where there has been a restriction and a sudden change from velocity head to pressure head, the maximum pressure head being just above the

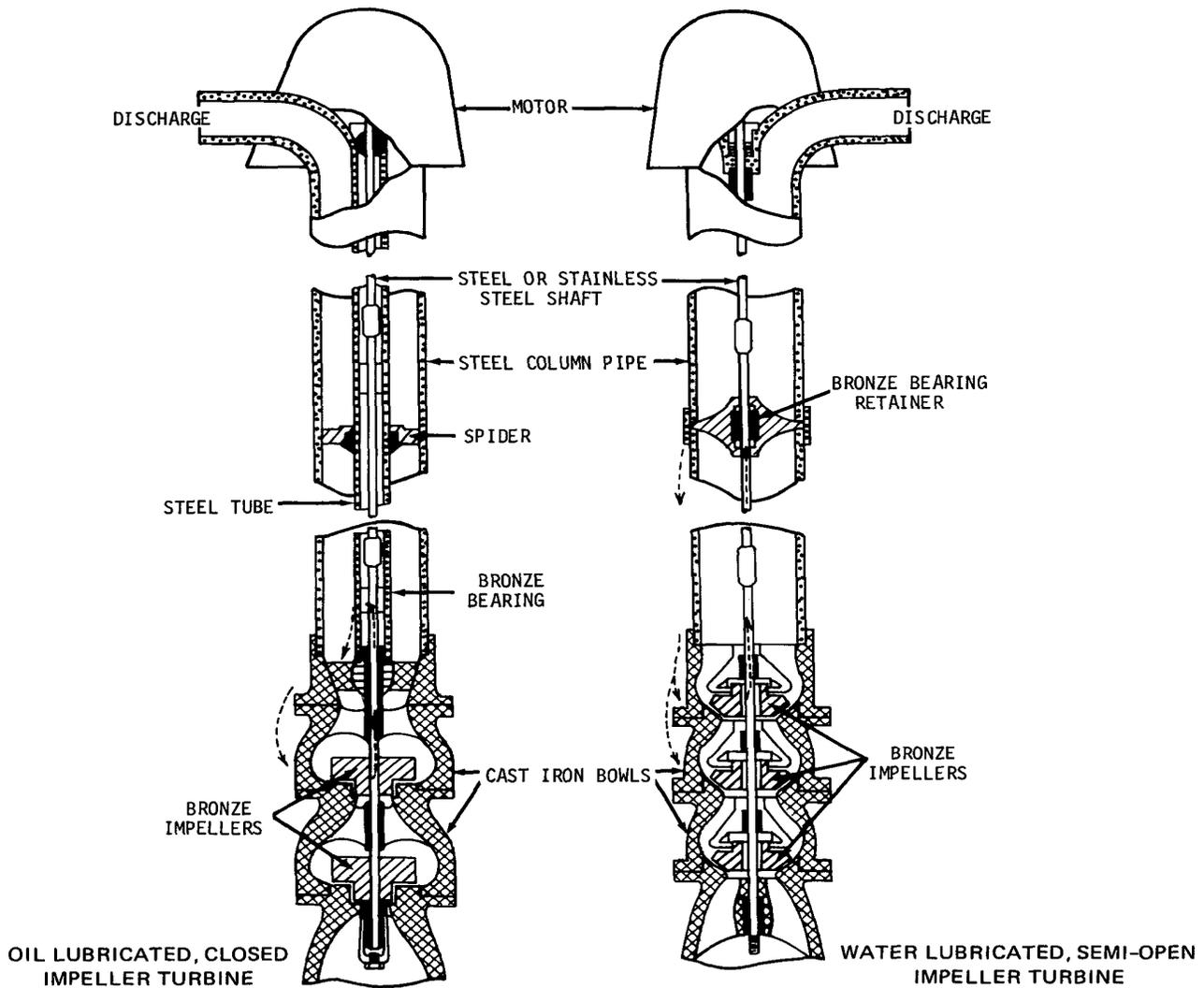


Figure A. Cross section showing areas within deep well pumps subject to corrosion attacks

turbine unit. (Similar pitting has also been noted within the turbine unit on the high pressure side of the guide vanes above the impellers.)

It can be assumed that gas bubbles are released from the water at low pressure points on the underside of the impellers, and at constrictions and eddies created by the extremely rapid changes in velocity, direction, and pressure within the turbine unit. As the water passes through each successive bowl, the gas bubbles and the water are subjected to increased pressure, and upon leaving the discharge bowl, the larger diameter of the column pipe converts the velocity head to additional pressure head. This pressure therefore provides a greater potential for solution of the

gas bubbles. Normally, the gases are nitrogen, carbon dioxide, and water vapor. As the carbon dioxide dissolves the water becomes excessively high in carbonic acid at the interface with the bubbles, because the acid diffusion rate in water is very low. As the acidic surfaces of the bubbles pass over the column pipe surface, corrosion is enhanced. As the water passes up the column pipe the bubbles eventually dissolve completely, and the interface is eliminated, thereby reducing the corrosion.

This type of attack has also been observed on the high pressure side of booster pumps, in valves, and elbows. The presence of dissolved oxygen or hydrogen sulfide can accelerate this type of corrosion.

Deterioration of Water Quality in Distribution Systems

T. E. Larson

A paper presented on Mar. 16, 1964, at the Missouri Section Conference on Corrosion, Columbia, Mo., and on Sep. 16, 1964, at the Chesapeake Section Meeting, Ocean City, Md., by T. E. Larson, Head, Chemistry Sec., State Water Survey, Urbana, Ill.

MOST annoying to all water utility personnel, as well as to the consumer, is deterioration of water quality that occurs between the plant and the household tap. Such deterioration takes place after plant treatment by acceptable practices at reasonable, if not insignificant, cost to the consumer. This is somewhat akin to serving him perfectly good drinking water in an unclean container.

The type of quality deterioration is not of concern to the consumer; anything less than a palatable, safe, and aesthetically pleasing water is neither expected nor accepted if he is paying the margin between the cost of water for fire protection and a quality product for household use. On the other hand, if he is not paying the necessary margin for a quality product, the consequences are of his own making.

Types of Deterioration

For analysis of quality deterioration, however, the type of deterioration is most important. For obvious reasons, the present discussion must be limited to water supply sources of reasonable quality. This can immediately eliminate a considerable number of sources. Moreover, certain types of deteriorations, such as red or black water result-

ing from oxidation by oxygen or chlorine of the natural iron or manganese in the water delivered to the system and deteriorations caused by bad cross connections and inferior household water-using equipment, may be temporarily put out of consideration. Other types of deterioration may result from historical or external causes, but it would be difficult to eliminate these without seriously limiting the objective of this discussion.

At household taps or at hydrants, the observable effects of deterioration are numerous. The water may be rusty, or, although it may be clear when drawn, subsequent reaction of soluble iron with dissolved oxygen from the air may cause it to become rusty. It may be turbid, red, white, or black. It may be temporarily milky white from dissolved gases. It may have a wide variety of odors. The water may be much harder than that entering the system. It may cause blue stains on bath fixtures or turn silverware black. It may contain white or red filamentous particles, or, at times, granular particles. Not infrequently, with or without obvious deterioration in quality, there may be a lack of pressure not only at the tap but also, and most dangerously, at the fire hydrant.

State of the Art

Although many developments are in the making and research studies promise further improvements not only in treatment practices but also in construction materials and distribution system design, knowledge of treatment has advanced far in the past quarter century. Langelier's saturation index, for example, has extended greatly the applicability of calcium carbonate stability as a means of corrosion control. Cement-lined cast-iron and steel pipe for corrosion control is now available at little or no greater cost than coal-tar-lined pipe. Other pipe materials are also available, and satisfactory means have been developed for relining cleaned pipe. New jointing materials have obviated the need for jute packings, which have been a source of much trouble, and new trenching machines can produce cleaner and quicker installations. Chlorination in its various forms is better understood. Use of activated carbon for reduction of taste and odor and incidental organics is not unusual. Better means of recarbonation for pH control are available. Coagulation theory and the use of coagulant aids is much better understood, so that a better quality water is more uniformly provided, even though there is much more to learn and to be applied. Other improvements, too numerous to mention, are also a part of modern practice.

Given the present state of knowledge, there is little reason for any new water distribution system to suffer from other than the rarer types of quality deterioration. The major problems of deterioration today should be almost wholly found in old distribution systems with any of a number of failings, in some cases abetted by inadequately equipped or operated water plants.

Disorders of Age

Water systems are more likely to be largely old than new, however. A distribution system designed many years ago often suffers from the presence of mud, alum, iron oxide, manganese dioxide, slime deposits, or tuberculation resulting from corrosion of poorly protected pipe. Mud may result in dirty or turbid water, loss in chlorine residual, growth of organisms, taste and odors, corrosion, or loss in carrying capacity.

Residual alum deposits, often with the microorganisms and turbidity supposed to have been removed during filtration, may cause loss in carrying capacity and increase corrosion and odor problems.

Iron oxide, deposited before iron removal was practiced, may require years before it can be removed, even with the aid of frequent intensive flushing. Such deposits can also permit the growth and eventual decay of iron bacteria, which entails red water and odor problems.

Manganese dioxide deposits have been responsible for loss in carrying capacity, and for black and even purple water, after excessive polyphosphate treatment with chlorination.

Slime growths of zoogloal masses can be so luxuriant that, without adequate water circulation and chlorination, chlorine residuals are lost, carrying capacity is lost, and taste and odor problems develop.

Pipe tuberculated by corrosion also suffers from loss in carrying capacity and causes a loss in chlorine residual. In every case, it is difficult to protect the pipe by calcium carbonate treatment or any other means of preventing red water. The degree of difficulty depends on velocity of flow and degree of dirtiness or tuberculation. Mechanical

cleaning of tar-coated cast-iron pipe rarely, if ever, is satisfactory in all respects for even a temporary period, unless a corrosion-resistant lining is applied.

Although these problems are termed as disorders of age, unfortunately they can and do exist in new systems and new additions to old systems—not because the state of the art has not improved, but often because of failure to apply the newer improvements in the

of what is being deteriorated by what. Consider a water distribution system for a municipality of about 50,000 population, delivering 5,000,000 gal (20,000 tons) per day to some 14,000 services under a pressure of 50–60 psi through some 100 mi of pipe buried at a minimum depth of 6 ft. The system consists largely of approximately 25,000 sections of 16–20-ft pipelengths and an equivalent number of joints, with some 1,500 elbows and tees, 1,200

TABLE 1
Amounts of Foreign Constituents in Hypothetic System

Item	Concn.—mg/l (Unless Otherwise Noted)	Tot. Amt. in System at Any Time—lb* (Unless Otherwise Noted)	Tot. Amt. Delivered Daily Through System—lb† (Unless Otherwise Noted)
Minerals	500	2,500	21,000
Iron	0.3	1.5	12.6
Manganese	0.05	0.25	2.1
Chlorine-ammonia compound residuals	0.3	1.5	12.6
Phenol	0.001	0.005	0.042
Acetic acid	5	25	210
Nitrogen	16	80	670
Oxygen	8	40	335
Methane	1	5	42
Excess CaCO ₃	1-10	5-50	42-420
Suspended matter	0.1	0.5	4.2
Ammonia	1	5	42
Deuterium oxide (HDO)	156	780	6,600
Radium ²²⁶	3 μC/l	6.8 g	57 g
Strontium ⁹⁰	10 μC/l	22.5 g	190 g
Coliform organisms	1 per liter	2,250,000 units	19×10 ⁶ units
Tot. organisms	100 per liter	220,000,000 units	1,900×10 ⁶ units

*Total amount of water is 5,000,000 lb (600,000 gal, 2,200,000 liters).
†Total amount of water is 42,000,000 lb (5 mgd, 19,000,000 liters).

art. Whether this be the result of negligence or penny-wise, pound-foolish decisions is not the object of this discussion. Rather, the object is to call attention to the nature of distribution systems, the problems that can exist, and their causes.

Hypothetic System

Before discussing deterioration further, it is important to have some idea

valves, and 900 attached fire hydrants. The system is designed to withstand external as well as internal shock stresses of several hundred pounds per square inch. In addition, water storage and pressure regulation would require one or two reservoirs, elevated or ground surface, with pumping facilities.

Materials in contact with the water may vary from metallic to mineral to organic; each can have coatings of

various compositions, thicknesses, degrees of adherence, and porosities, or natural surface conditions peculiar to the composition and the method of manufacture.

The system is designed for minimum standards for fire flows as well as adequate pressures to deliver water for domestic, commercial, and industrial uses. The normal velocity of flow may range 0–6 fps on a continuous or intermittent basis. It is not unusual that, in certain sections of the system, the water may remain between the point of entry and the point of withdrawal for several days.

The temperature of the water may range seasonally from near freezing to as much as 80°F. The temperature from the point of entry to the point of withdrawal may also vary several degrees, depending upon the season and the time the water remains in the system.

The volume of water in the system, exclusive of that in storage, is probably about 600,000 gal. This water may contain as much as 500 mg/l of assorted minerals, largely as ions, 1 coliform organism per liter, 100 other organisms per liter, 0.3 mg/l chlorine (as chlorine-ammonia compound residual), 1 μg/l phenol, 0.3 mg/l iron, 0.05 mg/l manganese, as well as a host of unknowns. The concentration of such constituents in the system at any time and the total amount transmitted per day are given in Table 1.

Foreign Components

Whether they are particulate suspensions or dissolved as a homogeneous solution, these foreign substances occupy space in the water. In solution, they are surrounded by water, being bonded with the water molecules, trapped in cages of self-bonded water

molecules, or suspended by virtue of low specific gravity and possible hydration.

Relative sizes of the components of water and foreign substances are given in Table 2. These indicate an order of relative spatial magnitudes. The volumes occupied may, generally, be assumed to be proportional to the cube of the components' diameters; hydration of precipitated hydroxides further increases the volume.

Equilibrium

Although most minerals are relatively stable in relation to each other, their ions are electrically charged and usually separated as the result of the

TABLE 2
Relative Sizes of Components of Water and Foreign Substances

Component	Particle Size—μ
H ₂ O(l)	0.0003
H ₂ O(g), O ₂ , CO ₂ , CH ₄ , N ₂	0.0004–0.0005
Ions	0.0002–0.0004+
Virus	0.01–0.5
Turbidity	0.5–10
Bacteria	0.3–30
Fine sand	20–200

high dielectric constant of water. Thus, these ions are in a state of constant attraction and repulsion amongst themselves within a liquid whose molecules also possess discrete positive and negative charges.

It is convenient to think that associations between ions and undissociated molecules are in equilibrium. This does not necessarily mean that the undissociated molecules are stable. Rather, dissociation of specific pairs of associated ions takes place and others become associated. This equilibrium relates more to the probability that a

APPENDIX B (Continued)

proportion of specific pairs of associated ions exist relative to the disassociated ions of the same species. It should be considered a dynamic state sensitive to such physical factors as temperature and to its elements' association with other species of ions.

Although equilibrium is a condition which, for practical purposes, may be said to exist, it should be recognized that it is a condition approached at an ever decreasing rate as the criteria for fulfillment are approached.

The number of water entities, if not associated with each other, would total about 5,000 times the various other entities. The water entities in themselves, particularly through their self-association, have a profound effect on interactions between the ionic species and on their rate of movement by diffusion. Thus, mechanical movement of the water body as a whole—as practiced in coagulation—promotes interreactions of the entities and enhances the approach to equilibrium.

Reactions

A distribution system, then, carries a liquid that is inherently dynamic, and continuing changes are in turn stimulated by the movement of the water through the system. Aside from simple chemical equilibria in solution, it is possible that new particulate matter may be formed from these reactions as solubility equilibria are approached. There can also be selective adsorption on inorganic or biologic particulate matter. There can be enzyme reactions within organisms and consequent contribution of new chemical ingredients to the water. The organisms may multiply under favorable conditions, or they may be starved to dormancy or to death and subsequent decay.

It is probable that all reactions of soluble entities with particulate matter are basically surface reactions, governed by diffusion and adsorption, or subsequent absorption, and therefore are dependent upon the dynamics of the system.

Of no less significance is the retaining interior surface of the distribution system, which constrains the water from entry to exit. Here, too, are many possibilities for surface reactions, likewise governed by diffusion and adsorption and dependent upon the dynamics of the system. In this hypothetical distribution system, with perhaps 1,300,000 sq ft of pipe exposed to water,¹ a gallon of water may be exposed to as much as 80,000 sq ft of pipe, or a single square foot of pipe may be exposed to 1 mgd.

Influent Quality

Today, when improved practices are changing treatment from an art to a fledgling science, quality failure is an especially important index of inadequacy of knowledge regarding treatment. Whether failures should be attributed to treatment practice, design, or condition of the system is not always apparent. Certainly, any or all of these factors could be causative; much remains to be known about all of them.

It is possible for coliform and other organisms to withstand treatment and pass into the distribution system. Treatment to condition the water against corrosion of poorly protected metals is still an uncertain science, complicated by changing conditions of usage and the various conditions of the different segments of the system.

Biologic Disorders

So, aside from disorders of age, there can also be disorders of what might be

called quality control. These fall into two broad categories: the microbiologic or biologic and the chemical.

Iron bacteria. The presence of these may be considered a disorder of age. Whether they are *Crenothrix*, *Gallionella*, or others; such as *Leptothrix*, iron must be present. It has been proposed recently that *Leptothrix* is a form of *Sphaerotilus* and can accumulate either iron or manganese.² In any event, iron bacteria should not be present in properly treated water in a clean distribution system.

Coliform organisms. The coliform organism is an indicator of pollution. Given a raw-water supply of reasonable quality with proper coagulation, chlorination at an adequate retention time, and a prescribed chlorine residual entering the distribution system, there should be no coliform organisms in the distribution system. Such treatment should also preclude the presence of typhoid organisms. In the absence of residual chlorine in a dirty system, however, coliform organisms can exist.

Other microorganisms. It is doubtful whether anyone will ever be able to enumerate all of the organisms that may be found in distribution systems. Nevertheless, a few have been found to produce deleterious effects on distribution system water quality. When such organisms are prolific enough to cause a slick, slippery coating or a visible slime on the pipe wall, a measurable chlorine demand should be produced by oxidation of the organisms or of their metabolic products. The demand may be so great that it becomes impossible to obtain chlorine residuals in the remote portions of the system except during high-velocity flushing.

Nitrosomonas. *Nitrosomonas* can develop as a slime on the walls of pipe.

This happens in the presence of ammonia and dissolved oxygen. The slime can slough off and appear at hydrants or at the household tap. Under anaerobic conditions, putrefaction can result in taste and odor problems. In waters containing high ammonia concentrations, breakpoint chlorination is impractical; for small systems, the pumping capacity and elevated storage are not sufficient to provide adequate flushing. The use of copper sulfate with chlorine-ammonia compounds serves to keep the growth in check. Lime softening to raise the pH also appears to prevent such growths. *Methanomonas* also reportedly produces slime, in the presence of methane and dissolved oxygen. There is, however, little documentary information on this subject.

Sulfate-reducing bacteria. These utilize the sulfate ion to form hydrogen sulfide under anaerobic conditions. Such conditions may occur at pipe joints, particularly in areas of low demand and low-flow velocities, even when dissolved oxygen is present in the body of the water flow. Such anaerobic conditions may prevail in the cores of tubercles and under any debris that may be in the system. The extent to which corrosion and tuberculation is thereby enhanced has yet to be evaluated. The resultant problems are tastes and odors, staining of silverware by hydrogen sulfide, and possible acceleration of corrosion and tuberculation.

Sporovibrio desulfuricans. This and other such sulfate-reducing organisms thrive better at moderate temperatures and in neutral or slightly acid conditions. In surface water, these temperatures prevail in all seasons except winter, and the low pH prevails in tubercles and debris under anaerobic

conditions. Chlorine can destroy the organisms, but it is virtually impossible for chlorine to penetrate tubercles and debris. These organisms can remain dormant for long periods even in the presence of dissolved oxygen. They must have some organic matter to grow luxuriantly; this could either be provided by dead cells in tubercles or absorbed from the distribution system water.

Beggiatoa. Sulfide-oxidizing bacteria thrive as a slime in the presence of hydrogen sulfide and dissolved oxygen, to form sulfur. The presence of such organisms might also be considered as a disorder of age, because adequately treated water in a clean distribution system should have no hydrogen sulfide.

Actinomyces. These have been reported as the source of taste and odor problems in heavily polluted water supplies and when putrefaction occurs on the banks of streams during low-flow conditions. In some instances, it has been reported that water which is odor-free after activated-carbon treatment becomes foul on passing through the distribution system, even in the presence of chlorine. The records are not clear on this problem, and much appears to be conjecture.

Vegetative organisms. Algae, *Crenothrix*, *Sphaerotilus*, and other vegetative organisms have also been reported in water mains. Crustacea such as water fleas, mollusks such as snails, nematodes, and other animals are not unusual. Whether all of these should be considered to cause deterioration of water quality in the mains or whether they are transient inhabitants is an open question. Certainly, their presence indicates an inferior water quality. It appears that water lice (*Asellus aquaticus*) may survive and

multiply in the system for long periods of time. Their removal can be stimulated by the use of phrethin and flushing.³

Corrosion

Deterioration of water quality through changes in mineral content can often take place as the result of "dirty" pipe, use of pipe poorly protected against corrosion, from treatment inadequate to reduce or prevent corrosion, or from circulation inadequate to aid in protection against corrosion. An absence of red water at the tap or hydrant is no assurance that the system is not suffering from corrosion or tuberculation. The greatest number of problems seem to be due to a combination of poorly protected pipe, poor circulation, and inadequate treatment.

Most corrosion problems are associated with relatively soft waters containing dissolved oxygen. The logical way to eliminate this problem would be treatment for oxygen removal; however, capital and operation expenses have been prohibitive.

As a rule, hard water is less corrosive than either water softened by lime or ion-exchange treatment or naturally soft water, particularly when dissolved oxygen is present.

A third class of treated waters also is notorious for suffering deterioration in the distribution system, whether such water has an appreciable hardness or not. These are coagulated and filtered surface waters. In too many of these instances, no doubt, quality problems result from the failure even to attempt to adjust the pH to a satisfactory level and provide a water that is "stable," or protective. There is evidence, however, that, in some cases, where the pH is not greatly different from the stable

level, few problems are experienced. In others, there is evidence that, with the best advised pH adjustment, even to a positive index of supersaturation with respect to calcium carbonate, problems are rampant.

There is little point in elaborating on principles of corrosion and its prevention, or on the validity of the theory and equations related to the solubility of calcium carbonate. There is more merit in focusing attention on the failures of sincere applications of the principle of calcium carbonate protection for distribution systems. They are not merely tormenting exceptions.

Tuberculation

Previous comments on dirty and tuberculated pipe and on velocity of flow probably require further elaboration. In the presence of dissolved oxygen, active tubercles can sustain themselves through production of hydrogen ions, as ferric hydroxide is precipitated. Such acidity, associated with a predominance of sulfate and particularly chloride ions in low-alkalinity water, eventually results in an actual acidic condition, if the buffering effect of the bicarbonate-carbon dioxide equilibrium is overcome. Thus, the proportion of chloride and sulfate to alkalinity is a factor related to the development and continued growth of tubercles and to corrosion in general.

The total alkalinity is also an independent and important factor, serving as a buffer to change in pH. Stumm⁴ has recently reviewed the effect of pH on the types of alkalinity and the resultant effect on the buffer capacity. It has also been shown that low alkalinity (<35 mg/l) offers little buffer effect on pH as the temperature is increased in hot water tanks.⁵ For such

waters, temperature change can reverse a positive to a negative saturation index.

The quantity of acidity developed by active tubercles can seriously decrease the pH in the area of the tubercles and nullify the designed favorable state of CaCO₃ supersaturation of the water at the surface of the tubercle.

Similarly, mechanical cleaning of pipe, by removing sections of coatings, increases the areas open to corrosion. Corrosion can then proceed at a rate greater than the rate of protection that can be expected from the water.

Flow Velocities

High velocities of flow are related either to the protection or the degradation of the quality, or both. Under laminar low flows, the lateral movement of ions and molecules from areas of high to low concentration at the pipe wall must be by diffusion. The rates of diffusion under the very low concentration gradient are extremely slow. At increasingly turbulent flow rates, the diffusion distance through the laminar layer at the pipe wall is decreased, and the corroding elements (dissolved oxygen and hydrogen ions or both) as well as the protecting elements (calcium and alkalinity) approach the pipe wall correspondingly more rapidly. If the corroding elements predominate, corrosion is accelerated; but if the protective elements predominate, protection is generated more rapidly up to the point of their depletion in distance or time. The higher velocities, of course, provide a greater quantity of corrosive or protective elements to the pipe wall per unit of time. These elements are therefore related to the development of active tubercles and their rate of corrosion or degree of activity.

Protective Deposits

Mention should be made of the amount of deposit required to protect uncoated surfaces. If 1 mi of 6-in pipe were to receive a uniform deposit of calcium carbonate 1 μ in thickness, the total weight of the deposit would be 5.85 lb. In terms of mils (0.001 in.), the weight would be 146 lb per mil per mile. Thus, even with a calcium carbonate concentration 10 mg/l in excess of solubility, more than 1.8 mil gal would have to be transmitted if all the excess calcium carbonate were deposited uniformly in a layer 0.001 in. thick from water on 1 mi of cleaned pipe. Such a flow in a short period of time is impossible at dead-ends.

McCauley's work on deposition of calcium carbonate as a thin transparent layer on clean steel and sand-blasted cast-iron pipe shows that such protection requires deposition be amorphous or microcrystalline rather than in the large, visible calcite form.⁶ His process involves an excess of calcium carbonate solubility of as much as 150 mg/l and the use of polyphosphate in a relatively small concentration (1–2 ppm) in combination with lime and soda ash at a flow rate of 4 fps for 2 hr. The phosphate seems to inhibit deposition of large crystals, thus providing a more continuous protective film, and to permit adherence to the metal wall.

From the observation of properly protected specimens, the deposition appears to be almost transparent. This is quite different from the usual "egg shell white" type coating. McCauley's coating appears to be the type that protects pinholes or holidays in tar-coated pipe in the same manner that so-called noncorrosive waters do. In many such cases, the pipe shows few points of

corrosion and the tubercles are very small and inactive.

Such noncorrosive waters are not treated with polyphosphates, however. It may therefore be deduced that these waters contain a natural ingredient that provides the same protective effect as the polyphosphate in McCauley's procedure. This natural ingredient might also be considered more versatile, for it does not appear to be as dependent on velocity and cleanliness of pipe surface. This deduction harmonizes with the observation that treated waters are difficult to adjust for corrosion control. Inasmuch as treated waters are designed to remove undesirable ingredients from the water, it is probable that such treatment also removes a desirable unknown ingredient.

Silica and Color

Two natural components that may possess this inhibiting property are silica and color. Too little is known about either. Silica could be in a poly-molecular form and color may also have similar combining properties. Such properties would be associated with disruption of crystal growth, the binding of colloidal microstructures to each other as a film, and the concurrent binding of these to the metal surface or its oxide. Or, again, they may prevent hydration of iron oxide as it is formed by corrosion.

This speculation is supported by observations by Turner and Campbell at the Non-Ferrous Metals Institute in England,⁷ where synthetic waters formed nonprotective calcium carbonate and zinc carbonate on galvanized iron, but natural water did not form such carbonates and did not corrode. When a natural organic extract, including color, was added to the syn-

thetic water, protection with a transparent deposit was achieved.

Conclusion

A distribution system is a sensitive, dynamic, living individual with its own peculiar characteristics, not just a network of tubes joined together. Although it may not always seem so, planning is needed to permit necessary quantities of water to reach the right places at the times they are needed. And again, although from this discussion it may not appear so, there is usually a plan to provide a quality product at the point of delivery.

Unfortunately, these plans often have proved weak and their aims have been interfered with by inadequate attention and control in design, construction, use, or maintenance, as well as lack of recognition of quality factors and of the necessary treatment for maintaining a nondegradable quality. The best attention must be given at all times to each link in this chain of endeavors, and to the coordination of all phases of supervision, including that essential called management, to achieve the desired objective: delivery of quality product to the consumer.

Perhaps most significant is the recognition that quality design, quality construction, quality protective measures, and quality treatment cannot be obtained from low-quality materials and personnel or an "or equal" that is often less than equal. Quality cannot be obtained at minimum cost. The distribution system represents about two-thirds of a water utility investment. The cost of the best quality pipe and other

materials is only a fraction of the cost of installation or replacement.

There is no question that water treatment practices vary and that some are more difficult to control than others because of the raw material, the source of supply. The mineral quality of some supplies, given the present state of the art, defies such treatment as would prevent all corrosion. Treatment can be adequate to provide an excellent product for the consumer at the plant outlet, but inadequate to overcome inferior protective measures in the distribution system. Therefore, new additions to the system must be of the best material. Old segments of the system that have proved to be inferior must be rehabilitated. None of these are achieved without substantial additional cost.

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Bacteria, Corrosion and Red Water

By T. E. Larson

MANY investigators have devoted years to the study of corrosion. Numerous phases of this complex problem have been solved or eliminated but many are left unsolved and are complicated by a variety of new as well as old factors—factors found to prevent corrosion in some cases and to increase corrosion in others.

The question is definitely one which involves chemical reactions,—reactions which are known to be possible but vary in rate and which can be stopped or aided by side reactions. “How fast does the reaction take place?” “How long will the reaction continue?” These two questions are answered by the controlling factors. Control the rate, and corrosion may be minimized or stopped.

The present day control consists of using a protective coating composed of a substance unreactive to water and oxygen. Perhaps the most elementary protective coating is a film of hydrogen constituting the overvoltage phenomenon.

It is well known that pipe effectively lined with enamel, cement, asphalt, or coal tar is not subject to metallic corrosion. In every case, with the possible exception of cement, the coating must be firmly adherent and without breaks or pinholes which have been pointed out to be often more harmful than if the pipe were not coated at all. Concentrated attack may take place at these points to pierce through the metal long before general corrosion could weaken the structure.

Softened or naturally soft water properly treated with lime soda, caustic soda, soda ash or sodium silicate has also been found to prevent metallic corrosion when a good adherent, unbroken calcium carbonate or silicate coating has been laid down and maintained. It is essential that this coating be complete and maintained.

A paper presented at the Illinois Section meeting, Urbana, Illinois, April 21, 1939, by Dr. T. E. Larson, Chemist, State Water Survey, Urbana, Illinois.

Oxygen becomes almost a necessary evil when it is essential that aeration be the means of iron and gas removal, or taste and odor control. Corrosion has been shown to take place almost in proportion to the dissolved oxygen content in natural water (1). On the other hand dissolved oxygen can also aid in the inhibition of corrosion (2, 3, 4) by aiding in the deposition of calcium carbonate with ferric hydroxide at the point of corrosion reaction. Here the question is tied up with the velocity of flow and the various concentrations of negative ions.

“Red water,” the cause of numerous complaints may be from either of two sources. Iron may be present in the raw water in which case there is no hope of alleviating staining and bacterial growths without removal of the iron by an accepted standardized procedure. The other source is by corrosion of the distribution mains or service lines. It may be well to state the question of the rate of corrosion in another way: “How much time is available for corrosion to take place?” This will be discussed later.

The plague, or should I say one of the plagues, of the water works man’s life, consists of placing a clear, colorless, odorless water into the distribution system at the plant and finding consumers complaining of obtaining dirty, red, smelly water from their tap. That’s discouraging.

Most Illinois waters are moderately hard or hard and unsoftened. The addition of chlorine or chloramine, frequently accompanied by iron removal is in most cases the only treatment used, if any. This is typically exemplified by the University of Illinois water. Here only two peculiarities may be noted. The alkalinity of 330 p.p.m. is greater than the hardness of 280 p.p.m. and ammonia nitrogen is present in the raw well water to the extent of 1.5 to 2.5 p.p.m. The sodium bicarbonate presence is not considered to be a decisive factor in connection with “red water,” but the ammonia content has been found to be a new if not a potent factor.

Treatment at the University plant consists of iron and gas removal by coke tray aeration, sand filtration, and chlorination. As it leaves the plant the water is iron free by test, has a chloramine content of more than 1.0 p.p.m. and has a dissolved oxygen content less than 8 p.p.m.

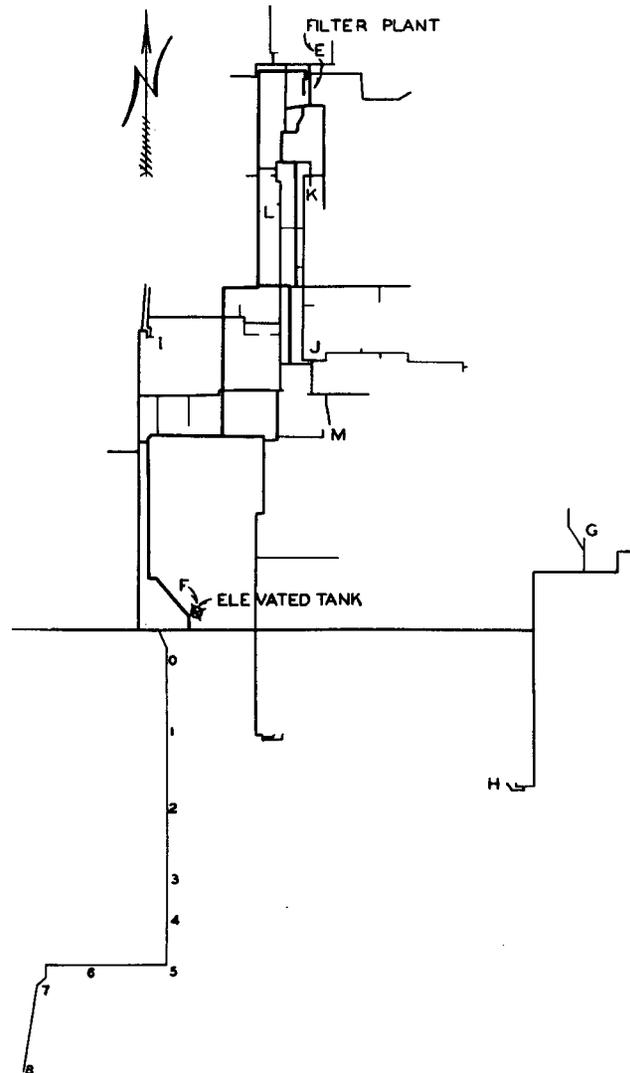


FIG. 1. University of Illinois Distribution System, exclusive of lines smaller than four-inch.

A rough diagram of the distribution system is shown in figure 1. Despite the condition of the water produced at the plant at the north end of the campus, frequent complaints of "red water" are received from various points throughout the system particularly at the south end two miles away. This condition could arise from two sources: first, from old deposits left in the mains before the treatment plant was installed; second, from present corrosive conditions in the mains. A rigorous flushing schedule has alleviated much of the trouble and has reduced complaints considerably, but the dilemma persists and at the far south "dead" end, iron water is had within twenty-four hours after flushing. Old deposits in the mains cannot fully account for occasional soluble ferrous iron content of as much as 8 p.p.m. Corrosion must at least in part be the answer here. Microscopic examination of "red water" sludge from service lines and of deposits in the mains has in no case disclosed the presence of iron bacteria.

In general, complaints increase with increasing distance from the plant. This is in part due to the fact that the velocity of flow decreases with increase in distance from the plant. The iron dissolved or the decrease in dissolved oxygen per unit distance traveled by a unit volume of water near the plant is far less than that at the outer ends of the distribution system. To establish a comparable time-basis, consider the time for one cubic foot of water to pass or come in contact with one square foot of iron surface.

Computation of Contact Time

As water leaves the University plant (1,250,000 gallons per day through a 14-inch main) the average time of contact for one cubic foot of water per square foot of pipe surface is 0.15 seconds. If corrosion does take place, the drop in dissolved oxygen is slight and the increase in iron per unit volume of water is relatively minute. As the water is drawn outward away from the plant it can be seen that the time of contact may approach infinity as the rate of flow approaches that of a "perfect dead-end." Assuming that one-sixth of the water reaches the south campus at the water tower, the time of contact per cubic foot of water (200,000 gallons per day through a 12-inch pipe) per square foot of pipe surface is 0.87 seconds or six times as much as at the plant. Continuing outward to a so-called "dead" end (1000 gallons per day through a 4-inch main) the time of contact is 58 seconds, or 400 times as much time is available for corrosion to take place and iron to be picked up by the water.

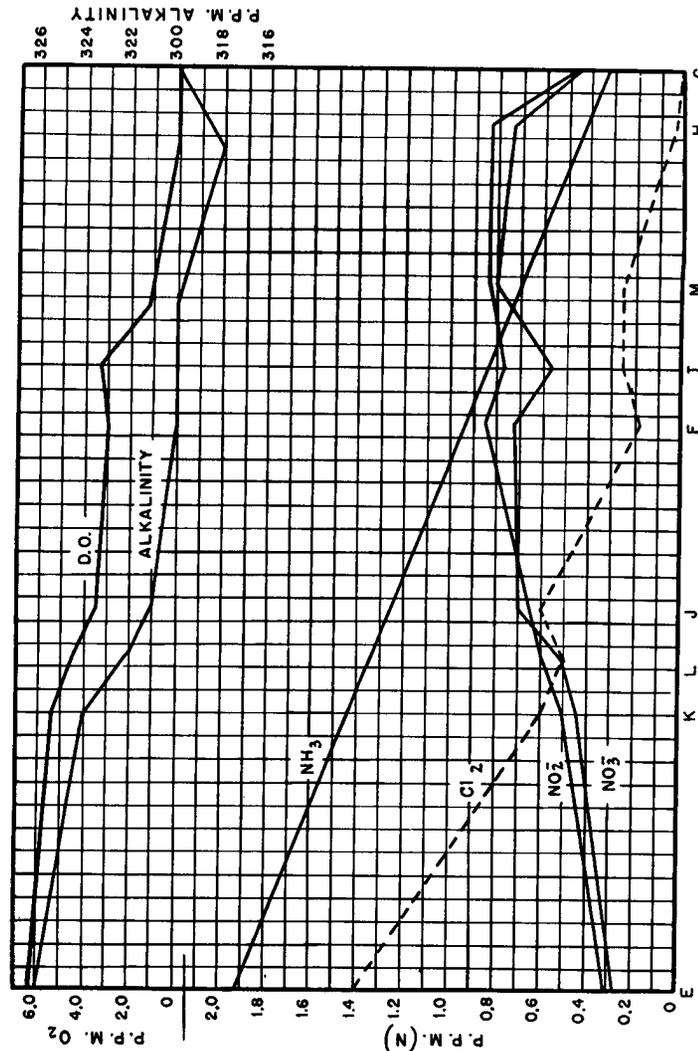


FIG. 2. Typical Variations as water is distributed from north to south ends of campus (left to right).

One other factor has been found to be present to affect the rate of corrosion. It has been noticed that a zeolite filter using the University water reduced the dissolved oxygen to zero. Further tests with a sand filter produced the same effect and it was also found that on passage through the filter that the ammonia content of the water decreased and the nitrite content increased. H. L. White, Sanitary Engineer of the University of Illinois, has noted an increase in the nitrite concentration on passage through the filters at the plant. Nitrite interference has been noticed in tests for chlorine at outer ends of the distribution system.

Accordingly seven series of analyses were made on samples of water collected from various points in the system. The constituents de-

TABLE 1
Typical Trend of Data Throughout Distribution System
(Results in parts per million)

	D	E	K	J	L	F	I	M	H	G
	FILTER EFFLUENT	FILTER PLANT SERVICE	CHEMISTRY BLDG.	NEW AGR. BLDG.	WOMEN'S BLDG.	ELEVATED TANK	HUFF GYM	DAIRY MFG.	ROUND BARRNS	PREXY HOME
Ammonia - N	1.92	1.92	1.44	1.26	1.34	.94	.84	.70	.42	.34
Nitrite - N	.23	.32	.50	.65	.60	.85	.77	.85	.84	.46
Nitrate - N	.26	.28	.44	.70	.52	.72	.56	.80	.74	.45
D.O.	6.3	6.2	5.4	3.4	4.4	3.0	3.4	1.2	0.0	0.0
Cl ₂	1.8	1.4	.6	.6	.5	.18	.25	.25	.03	0.0
Fe	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	.62	.08
Alk.	326.	326.	324.	322.	321.	320.	320.	320.	318.	320.
6 da. 20°C. bact. count	0	0	0	0	26	600	5000	2000	1600	1500

termined included ammonia, nitrites, nitrates, dissolved oxygen, free chlorine, iron, alkalinity, and 37° and 20° incubation bacterial counts. A typical series is indicated in table 1 and fig. 2.

In general the data indicate that with increasing distance from the plant, the dissolved oxygen, the ammonia, and free chlorine decrease while the nitrites, nitrates and six-day, 20° bacterial count increase. Figure 2 indicates the trend in values with reference to the ammonia content.

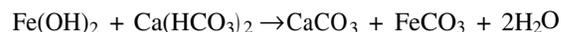
In order that ammonia be oxidized to nitrites or nitrates the ratio of the loss in dissolved oxygen to the loss in ammonia-nitrogen must

APPENDIX C (Continued)

be 4.0 or 5.15 respectively. In no case was this ratio less than 4.0. The average ratio was 6.0. Thus it may be deduced that no more than one-third and possibly not less than one-sixth of the oxygen is lost to corrosion. For the greater part it is used in converting ammonia to nitrites and nitrates.

Ammonia oxidation to nitrites has been reported (5, 6, 7) previously to take place in filter beds when ammonia was used in conjunction with chloramine. With ideal conditions for bacterial growth it has been attributed and later shown by Feben (8) to be due to bacterial action. Cultures of these bacteria, specific in their ability to convert ammonia to nitrites, have been isolated from the filter beds by Feben. These bacteria were found to be resistant to 2.0 p.p.m. chlorine. No concentrated effort has been made in this study as yet to isolate these bacteria since they will not grow on ordinary media and are difficult to isolate. Despite the ordinary Standard Methods 37° counts and coliform test results of zero, the 20° counts can be consistently shown to be over 1000 bacteria per c.c. at certain localities in the system. At least some twenty different types of bacteria other than these are known to be present in the system. Also, many years of previous study by the State Water Survey on the action of nitrifying bacteria have shown the action indicated in this study to be undoubtedly bacterial.

A slight but definite general decrease in alkalinity is noted. Were it not for the consistency of this trend, it would be attributed to inconsistency in the raw water alkalinity. However, in no one series of the tests made was the alkalinity in the system greater than or equal to that of the filter effluent. This would indicate a slight deposition of calcium carbonate in conjunction with corrosion by



to give calcium carbonate in conjunction with ferrous and ferric oxide. Then too, any bacterial growth requires a source of carbon such as carbon dioxide. Calcium carbonate deposition is further confirmed by analysis of deposits collected from a north campus main in September, 1938. The analyses indicated that only one of every seventeen ferrous iron equivalents is replaced by calcium carbonate. Due to the high rate of flow at this point, the iron that goes into solution per volume of water is very slight and undetectable by analysis.

Corrosion at this main was not noted to be particularly severe but it was definite and of two forms. Small, single and collective tubercles were noted having their origin at pinholes in the bituminous lining. These were hard, compact and often grown together, and were easily picked off with a penknife. Loose, slimy, black mud appeared at pipe joints and extended to either or both sides of the joint for various distances. Its source is quite possibly due to deposits laid down before the treatment plant was installed to remove iron and traces of hydrogen sulfide. Galvanic action may enhance corrosion here, but the fact that a strong hydrogen sulfide odor was given off from acidified samples of this mud indicates some old deposition. This mud as well as the tubercles was coated on the water side by a hard, yellow-brown crust. The velocity of flow here was quite high and after aeration was installed, the dissolved oxygen was rapidly fed to the ferrous oxide on the pipe walls to produce the ferric oxide-calcium carbonate crust. This outer coating does not appear to be sufficiently impermeable to prevent corrosion but appreciable inhibition is afforded.

In connection with bacterial action it is interesting to note that although the dissolved oxygen is partially used up in oxidation of ammonia instead of corroding the iron, this oxidation converts a basic ion into an acidic ion thereby producing two equivalents of acid from one equivalent of a neutral salt. In other words, the loss of one ammonia equivalent produces two free acid equivalents.



Although bacterial protoplasm contains some three and one-half times as much carbon as nitrogen and some of the free carbon dioxide is used up here, only a very small percentage of the ammonia loss is converted to protoplasm. Consequently little of the carbonic acid produced is used up in this manner.

Although the ammonia lost per volume of water is slight, the acidic condition can be expected to be greater at the pipe walls where the bacteria are to be found. This permits two corrosion enhancing conditions. First, a decrease in the protective action of calcium carbonate and ferric oxide is to be expected. Second, oxidizing agents are available to continue corrosion in lines where the dissolved oxygen is depleted. The latter effect is exemplified by the conditions in the far south "dead" end of one mile length. The dissolved oxygen

entering this main is less than 1 p.p.m. and is rapidly depleted. Nevertheless the iron at the exit has been found to be as high as 8.0 p.p.m. In the meantime nitrites and nitrates are reduced from 1.0 to 0.1 and from 0.7 to 0.2 p.p.m. respectively (table 2 and fig. 3). The data in this figure are plotted according to distances in feet as

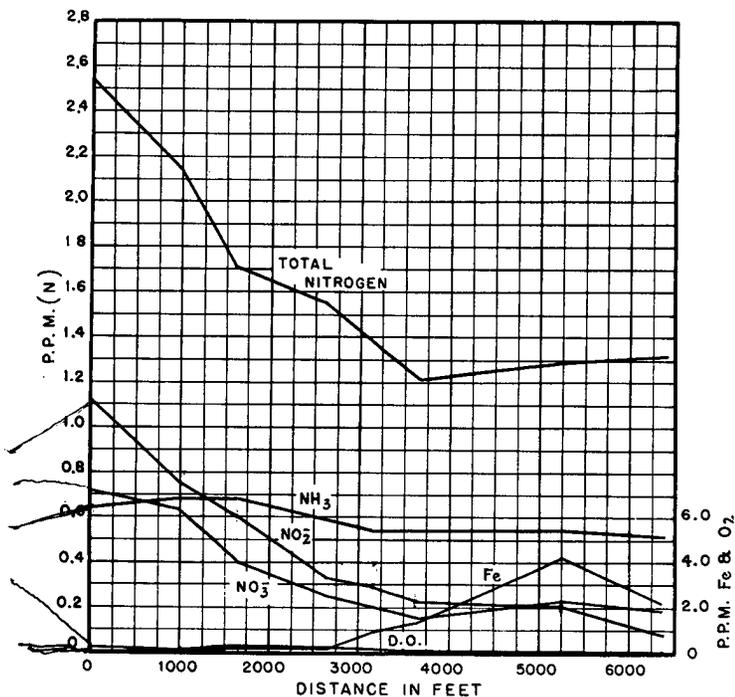


FIG. 3. Typical Variations in "dead" end (four-inch) after oxygen is depleted. (73 sec. per cu.ft. water per sq.ft. pipe surface).

measured between sampling points. Here anaerobic bacterial action is strongly suggested.

Perhaps it should be mentioned that analyses for such low concentrations of ingredients showing such low differences in magnitude are sometimes questionable but the consistency and direction of change in these constituents nullifies any doubt of their validity.

Summary

A certain water may be only slightly corrosive in one part of a system and strongly corrosive in another due to the difference in time of contact for corrosion to take place per unit volume of water. The concentrations of chemical constituents affecting the rate of corrosion can change during passage through the system to alter the rate which controls corrosion. A classification of waters as corrosive and not corrosive cannot be made without placing restrictions on all factors affecting the rate.

Dissolved oxygen in this water system gives rise to conditions which may inhibit or enhance "red water." Inhibition is experi-

TABLE 2
Typical Low Flow Data
(Results in parts per million)

	SAMPLING POINT							
	0	1	2	3	4	5	7	8
Ammonia - N	0.64	0.68	0.68		0.54	0.54	0.54	0.52
Nitrite - N	1.12	0.75	0.60	0.33	0.29	0.22	0.21	0.08
Nitrate - N	0.72	0.63	0.39	0.25	0.2	0.15	0.23	0.19
Kjeldahl - N	0.70	0.76	0.72	0.98	0.88	0.84	0.84	1.04
(Kjeldahl + nitrite + nitrate) - N	2.54	2.14	1.71	1.56	1.37	1.21	1.28	1.31
D.O.	0.2	0.1	0.2	0.2		0.0	0.0	
Alk.	318.	318.	320.	314.	316.	316.	314.	314.
Fe.	0.	0.	.08	.08	.88	1.32	4.16	2.16

enced by the formation of a more or less protective ferric oxide-calcium carbonate coating in the mains which can hinder penetration of dissolved oxygen to the metal itself as well as prevent corrosion products from sloughing off. The presence of ammonia and oxygen as a source of energy for bacteria gives rise to bacterial growths in the mains. Corrosion is enhanced by the bacterial transformation of basic ammonia and oxygen to acidic and oxidizing nitrites and nitrates.

The determination of the depletion of dissolved oxygen throughout this system is not a true measurement of the degree of corrosion. Depletion of dissolved oxygen at the "dead" ends and service lines of the system gives rise to a condition where ferrous iron is not

APPENDIX C (Continued)

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oxidized to insoluble ferric oxide and solution of iron to the ferrous state takes place at the expense of the nitrite and nitrate previously formed—quite possibly by bacterial action.

What corrosion that does take place in the system as a whole is magnified by the accumulation of traces of the iron in the gelatinous masses of bacterial growths clinging to the pipe in localities where the velocity of flow is low and sloughing off occasionally.

We are deeply indebted to Mr. White and his staff at the water plant without whose splendid cooperation a study in this manner could not have been accomplished.

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