EFFECT OF WATER QUALITY
PARAMETERS ON CORROSION OF MILD STEEL,
COPPER AND ZINC

BY

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL
OF THE UNIVERSITY OF FLORIDA IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1981
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By

Abdul Baqi Ahmadi
In the Name of God, Most Gracious, Most Merciful

To the real "Mujahideen," who are striving in the cause of truth, to get rid of injustice, oppression, mischief and international terrorism of all forms. May Almighty God give them victory in their just struggle.
ACKNOWLEDGEMENTS

I wish to gratefully acknowledge the expert guidance, constructive criticism, understanding and friendship of my committee chairman, Dr. John Edward Singley, without whose technical and financial support this work would never have been completed.

I am sincerely grateful to Dr. John Zoltek, Jr., Dr. Eric R. Allen, and Dr. Dinesh O. Shah for their friendly advice, valuable instructions and contributions to my education at the University of Florida.

A special thanks goes to Miss Shirley A. Jordan for her numerous contributions to completing this research project. The laboratory assistance of Patricia Singley, Lee Persia, Charles Dougherty, and Mark Halverstadt are greatly appreciated. I have accumulated many debts while attending the University of Florida that remain to be acknowledged. The many suggestions of Dr. Edwin Pyatt, Chairman of the Department of Environmental Engineering Sciences, the valuable advice of Dr. Herbert Bevis, and the cooperation of Mrs. Eleanor Humphries and Miss Barbara Chamblin in administering this project are gratefully acknowledged. The professional assistance of Mr. Richard Tomlinson in constructing the stirring apparatus is sincerely appreciated.

Many thanks are due Miss Judy Judd for her expert typing of this manuscript.

I would also like to express my gratitude to the U.S. Agency for International Development for partial support of my training, and
particularly to Dr. Richard Downie, Director of International Student Services, for his valuable counsel.

The technical assistance of Ting-Ye Lee in running computer programs on the North Regional Data Center (NRDC) computer facilities is gratefully acknowledged. I am sincerely thankful to Dr. Marvin Gardels of the U.S. Environmental Protection Agency, Division of Water Supply Research, for sponsorship of this study.

I am deeply indebted to my wife, Sanum J. Benti Alhaj Habibullah Khan, for her inspiration and outstanding support of my studies. Finally, to my dear parents, I wish to acknowledge a long overdue debt for their love, patience and true guidance throughout the years of my life.
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Abstract of Dissertation Presented to the Graduate Council of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

EFFECT OF WATER QUALITY PARAMETERS ON CORROSION OF MILD STEEL, COPPER AND ZINC

By

ABDUL BAQI AHMADI

August 1981

Chairman: John Edward Singley

Major Department: Environmental Engineering Sciences

Corrosion of metals in potable waters due to their health and economic implications is of great importance, both to the water industry and to the consumer. Research was conducted to determine the effects of various water quality parameters on the rates of corrosion of mild steel, copper and galvanized steel.

The impact of corrosion, the fundamentals of corrosion, causes and types of corrosion, methods of measurement and mitigation of corrosion, the occurrence of corrosive waters and their chemical composition, as well as piping materials and regulations concerning corrosion were presented in a thorough review of the subject of corrosion as related to drinking waters.
A multi-component stirring apparatus was designed to collect the data. Pourbaix diagrams were constructed and correlated with measured $E_H$ values. The rates of corrosion were measured using weight loss and electronic means. The water qualities were monitored for metal pick-up due to corrosion.

Dissolved oxygen was found to be a requisite for the corrosion of mild steel and zinc. Chlorine was found highly detrimental to copper, and dissolved oxygen was the second most important factor in copper corrosion. Dissolved oxygen and chlorine had a synergistic effect on the rates of corrosion of all metals. The role of pH was relatively minor, while $E_H$ values correlated positively with corrosion rates. Chloride and sulfate ions were both found to promote corrosion of all metals, while alkalinity in the presence of other ions inhibited corrosion. Chloride was more harmful to copper than to the steel. Natural color had a negative effect on the corrosion of steels and a positive effect on the corrosion of copper. Exposure time was found to affect the rates of corrosion, especially in weight loss calculations. Weight loss and electronic tests data correlated well in mild steel tests. Their correlation was poor in copper experiments.
CHAPTER ONE
INTRODUCTION

Water, our most precious resource, is an absolute necessity for both plant and animal life, provided it is free from toxic contaminants. There has been a growing interest in recent years in the safety and health implications of the water we drink. This concern is evident from the passage of the Safe Drinking Water Act, PL 93-523, which requires that the water quality regulations be met at the consumer's tap.

While for the most part, water utilities have supplied customers with waters of good quality, there are instances in which the quality of water has deteriorated drastically in the storage and distribution systems. Results of national surveys of drinking water systems indicate that 50 to 70 percent of the water utilities are distributing corrosive waters to their customers in the United States (1).

Corrosion, among other factors, is believed to be a major cause of water deterioration in the distribution systems and is considered as a main source of adding undesirable contaminants to the finished water. Some of the corrosion by-products are highly toxic and harmful to health, such as lead and cadmium (primary contaminants), while others have only aesthetic and economic significance. The latter include copper, zinc and iron (secondary contaminants).

The materials most commonly used for conveying potable waters include cast iron, mild steel, copper, galvanized steel, concrete and
asbestos cement. In addition to these, stainless steel, brass, bronze, aluminum and plastics are also employed in pumps, valves, hydrants and other appurtenances.

Although there have been major achievements in the development of many corrosion-resistant materials, their cost and availability is a prohibitive factor in potable waters and therefore, the large scale use of these materials is rather limited.

Due to the heterogeneous nature of the water quality and the distribution systems, the extent of corrosion and the resulting damages are also highly variable and unpredictable. Many corrosion indices have been developed in the past, but each one has serious limitations and is only applicable to specific cases.

While many experiments have been conducted on the corrosion of selected metals and alloys in specific environments, a comprehensive study of corrosion of metals in drinking waters of variable qualities is virtually absent. No data are available on the corrosion of metals in drinking waters that correlate the water quality parameters with the rates of corrosion of the metals involved.

In addition, on July 19, 1979, Environmental Protection Agency proposed amendments to the National Interim Primary Drinking Water Regulations for corrosion control. The amendments were necessary due to the adverse impact of corrosion on health, economics and aesthetic quality of drinking waters. This in turn intensifies an urgent need for further research and a better understanding of corrosion problems in public water supplies.
This research was initiated with overall objectives to (1) study the effects of various water quality parameters on the rate of corrosion of metals that are commonly employed in distribution and plumbing systems, (2) evaluate the effect of specific ions on the rates of corrosion, and (3) develop appropriate chemical control measures of water quality to mitigate corrosion.

More specifically, the effects of pH, dissolved oxygen, chlorine residual, natural color, alkalinity, chloride, sulfate and the total mineral content of the water on the rates of corrosion of mild steel, copper and galvanized steel were investigated. Those parameters that enhance or inhibit the rates of corrosion of these metals were identified.

Since corrosion experiments are normally time-consuming, a forty-eight unit multi-compartment stirring apparatus was designed to facilitate the accumulation of the required data.

The rates of corrosion were determined using the conventional weight loss method and an electrochemical technique employing Corrator* probes. In addition, the water quality was periodically monitored and the changes in the water quality were correlated with the rates of corrosion of the metals involved. Pourbaix diagrams were constructed for the metals under investigation to allow the comparison of the laboratory data with the theoretical thermodynamic aspects of corrosion.

* Corrator, Magna Instruments, a Division of Rohrback Corporation, 11861 East Telegraph Raod, Santa Fe Springs, CA 90670
In order to allow control of the variables, most experiments were conducted on freshly prepared synthetic water solutions, using deionized water and analytical grade reagents. Some experiments were performed on actual tap waters. The findings of this research will be highly useful in identification of the causative factors of corrosion. By modifying, eliminating or substituting the corrosion-causing water quality parameters, it is anticipated that corrosion in potable waters can be reduced with minimum effort and cost to both the water purveyors and to the ultimate consumers. The control of corrosion would result in protection of public health and substantial cost savings.

**Adverse Effects of Corrosion**

Water, as a universal solvent, has the ability to dissolve any material with which it comes in contact. The degree of dissolution of a material by water is greatly influenced by the stability of each material in water and by the presence of organic and inorganic substances, as well as dissolved gases in the water. Adverse effects could be broadly classified into three main categories: (1) Health effects, (2) Economic effects, and (3) Aesthetic effects.

**Health Effects**

The adverse impact of corrosion on health is primarily due to the addition of contaminants to the treated water by the corrosive action of water on pipes and plumbing fixtures. The most common of these contaminants include lead and cadmium, both of which may be dissolved from galvanized pipes used for plumbing. The former may also reach the consumer through the use of lead based solders and lead service pipes.
that are still in use in certain parts of the country. Both lead and cadmium are toxic metals and their addition to water as a result of corrosion, poses a threat to the public health.

Lead is a nonessential element for man and is a known toxic substance. Because of lead's low melting point and availability, man has utilized this material for many centuries (2,3). During the Roman Empire, lead was used for water pipes. Today, lead is commonly employed for manufacturing storage batteries, pigments, ammunition, solder, radiation shields and caulking (2,4).

Lead poisoning (plumbism) is not a new problem. Many instances of lead poisoning via action of water on lead pipes in U.S. water supplies have been reported in the literature (3). In the U.S., nine cases of lead poisoning due to corrosion of lead have occurred in different cities in Massachusetts in the early part of the twentieth century. At least one case of lead poisoning has been reported in Rhode Island, New Hampshire and Atlantic City, New Jersey (3,5-9).

Lead in drinking water originates from the corrosion of lead pipes and lead-based solders. A national survey of 539 water distribution systems in the early twentieth century, covering 41 states, concluded that 48 percent of the systems surveyed contained lead pipes (3). When aggressive water is distributed through lead plumbing, high concentrations of lead may reach the consumer as the result of lead corrosion. Available data indicate (10-16) that the National Interim Primary Drinking Water Regulations (NIPDWR) standard for lead has been exceeded by well over an order of magnitude in many distribution systems containing lead pipes. Results of surveys of several drinking water systems for lead corrosion are summarized in Table I.
Table I. Lead Levels in Drinking Waters (16)

<table>
<thead>
<tr>
<th>Location</th>
<th>Maximum Lead* Concentration, mg/l</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boston, Mass.</td>
<td>1.51</td>
<td>10</td>
</tr>
<tr>
<td>Worcester, Mass.</td>
<td>1.90</td>
<td>11</td>
</tr>
<tr>
<td>Marlborough, Mass.</td>
<td>0.17</td>
<td>12</td>
</tr>
<tr>
<td>Chatham, Mass.</td>
<td>3.00</td>
<td>13</td>
</tr>
<tr>
<td>New Bedford, Mass.</td>
<td>0.36</td>
<td>14</td>
</tr>
<tr>
<td>Benningten, Vt.</td>
<td>3.14</td>
<td>15</td>
</tr>
<tr>
<td>Seattle, Wash.</td>
<td>0.25</td>
<td>16</td>
</tr>
<tr>
<td>Victoria, B.C., Canada</td>
<td>0.10</td>
<td>16</td>
</tr>
<tr>
<td>Oslo, Norway</td>
<td>0.26</td>
<td>16</td>
</tr>
<tr>
<td>Glasgow, Scotland</td>
<td>0.86</td>
<td>16</td>
</tr>
<tr>
<td>Sutherland, Scotland</td>
<td>2.00</td>
<td>16</td>
</tr>
</tbody>
</table>

*U.S. EPA lead MCL is 0.05 mg/l.

Long-term ingestion of lead can cause severe health problems, even in minute quantities, because lead is a cumulative poison (16). Some of the adverse health effects of lead on man include anemia of plumbism, acute abdominal colic, acute and chronic encephalopathy, peripheral neuropathy, and late or chronic lead nephropathy in children and adults (2, 17). Other effects include pulmonary, endocrine, reproductive and renal cancer (2). Lead poisoning in general involves three organ systems: the nervous, the renal and the hematopoietic systems (2). The public health significance of lead in drinking waters and the correlation between lead levels and impaired health have been thoroughly reviewed by Patterson and O'Brien (16). Lead has been shown to cause hyperactivity,
hypertension, mental retardation and renal insufficiency in humans as noted in several studies involving drinking waters. Available data suggest that children and young adults are particularly susceptible to lead poisoning (16-21). Classic examples of lead poisoning by drinking waters have also been reported by Sedgwick (22) and Forbes (23).

The National Academy of Science in a series of studies on drinking water and health has recommended lowering the lead MCL to 0.025 mg/l, because of the adverse health effects of lead on man (24, 25).

Cadmium, like lead, is a cumulative toxic substance. It is a relatively rare element. Most cadmium is obtained from lead and zinc sulfide ores. Cadmium is not found pure in nature and is always present as an impurity in zinc. The cadmium content of zinc that is used for galvanizing varies from 0.005-0.75 percent (26). Versar in 1974, reported that the cadmium content of zinc that is used for zinc coating is 0.2 percent, and further reported that all of the cadmium from the galvanized coating is released to the environment due to corrosion in 4 to 12 years (27). The principle uses of cadmium include electro-plating (auto industry), pigments and chemicals, plastic stabilizer - PVC, alloys and solder, nickel, cadmium batteries, semi-conductors and pesticides (28).

The concentration of cadmium in drinking waters is usually low. In 1970, McCabe et al. (29), in a survey of 969 community water supplies, reported that 0.2 percent of 2595 distribution samples exceeded the 0.01 mg/l cadmium standard. The maximum concentration of cadmium was reported to be an unusually high value of 3.94 mg/l. In another survey of 720 water samples from U.S. rivers and lakes in 1970, it was found that 42
percent of the samples contained between 1-10 ng/g of cadmium, and only 4 percent were higher than 10 ng/g (30).

The sources of cadmium in drinking waters are galvanized steel, silver-based solders used with copper plumbing (31, 32), and plastic pipes (33). The main target organs in humans for the toxic effects of cadmium are the gastrointestinal tracts, the lungs and the kidney (31). The harmful effects of cadmium include osteomalacia (bone damage), hypertension, anosmia (loss of smell), dental caries, anemia, and effect on liver and nervous system (28, 31).

Some of the physiological effects of cadmium on man are nausea, griping pain, loss of appetite, vomiting and diarrhea (34, 35). A classic example of cadmium poisoning in humans is the well known "itai-itai" disease that struck some 200 residents along the Jintzu River in Japan, half of whom died (36). The river water was contaminated with cadmium released from a mine that produced lead, cadmium and zinc. The contaminated water was used for growing rice. The rice consumed contained up to 1.0 ppm of cadmium (28, 35, 36).

It is important to note that both cadmium and lead interact with other essential elements once they are ingested. These interactions have been shown to be antagonistic in some cases but competitive in others (37). This means that both cadmium and lead inhibit a metabolic process that depends on essential elements and exert their toxic effects. On the other hand, the presence of such essential elements as Ca, Zn and Fe can compete with lead and cadmium and thus retard the harmful effects of these toxic elements. For example, it has been reported that high Cd/Zn ratio may contribute to hypertensive cardiovascular disease (37),
while a lower Cd/Zn ratio has been shown to retard the toxic effect of large doses of cadmium in some experiments (38). Cadmium intake also has been shown to decrease copper and iron retention in the body and thus affect their metabolism (37).

The presence of both calcium and iron has been reported to interfere with cadmium and inhibit its toxic effects (39-41).

Exposure to lead has been shown to affect iron metabolism (42-44), and zinc has been reported to reduce the toxicity of lead (43, 45). Likewise, copper content in the body is depressed by exposure to lead (43). Calcium intake has been reported to inhibit lead absorption (46). The ingestion of lead and cadmium together has been reported to have caused increased teratogenic effects on experimental animals (47).

Another health aspect of drinking water is the controversial issue of water hardness and the incidence of cardiovascular disease (CVD). A great deal of research has been conducted in the past two decades, to determine if the water quality, particularly water hardness and health are interrelated. There is considerable difference of opinion among scientists about this subject, as reported in the literature.

Schroeder (48-50) has reported that a highly significant correlation exists between average water hardness by state and death rates from CVD. Furthermore, he demonstrated that calcium and magnesium were responsible for the inverse correlation with CVD as opposed to sulfate-carbonate ratio. Other investigators (51-55) have supported Schroeder's hypothesis that areas with harder waters had lower CVD death rates compared to the soft water regions.
Factors other than hardness of drinking waters that may affect CVD death rates have been reviewed in several articles (56-59). Some investigators question the validity of Schroeder's hypothesis that hard water and CVD death rates are inversely correlated (60, 61). A recent report (62) in the Journal of American Medical Association (June 20, 1980) contends that the widely accepted view that hard water protects against heart disease is probably incorrect. The report adds that no major change in the U.S. water hardness took place between 1968 and 1979, while there was a remarkable decline in CVD mortality (62).

The metal ions picked up by corrosive waters (Pb, Cd, etc.) and the deficiency of Ca, Mg and other essential elements may be considered as a main factor in high CVD incidences in soft waters, because soft waters are low in calcium and magnesium.

Economic Effects

Corrosion has been cited in the literature as "... our 51st State..." (63:7), and as "our national financial disgrace" (64:41) by some enthusiastic authors. Corrosion takes its annual tolls from all industrial applications and is a major cause of concern for many metal users. The annual cost of corrosion in the U.S. is more than the combined cost of floods, fires and hurricanes (63).

The direct cost of metallic corrosion in the U.S. was estimated by Uhlig in 1949 to be 5.5 billion dollars (65). The economic significance of corrosion in the U.S. has been reported by a number of other studies. Liechtenstein (66) estimated the annual cost of corrosion to be 10 billion dollars in the U.S. in 1966. In a study released by the National Bureau of Standards in 1978, the cost of metallic corrosion in the U.S. was estimated at 70 billion dollars or 4.2 percent of the gross national product for the year 1975 (67).
Although it is difficult to ascertain the exact cost of corrosion in different segments of various industries, the annual cost of corrosion in potable waters has been estimated at 700 million dollars by Ryder (68). This cost is usually for the corrosion of distribution systems, and it is believed that the cost of interior plumbing systems is far greater than the cost of distribution systems. In Seattle (69), the estimated annual cost of corrosion was 7 million dollars for household plumbing systems as compared to 400,000 dollars for the distribution system.

In another study, corrosion-related costs were estimated to be about 6 percent of the total water plant operating costs (70). The cost of replacement for U.S. community water supply distribution systems has been estimated to be as low as 17 billion dollars (71) with other estimates of 25 billion dollars (72) to as high as 125 billion dollars (73).

The cost of corrosion is made up of the replacement costs, painting, alloying, coating, cathodic protection, increased pumping costs due to loss in carrying capacity of pipes, labor and equipment costs, chemical costs for corrosion control, cost of lost or contaminated products as well as the cost of excess capacity and corrosion allowance in design of the systems (74).

**Aesthetic Effects**

The aesthetic significance of corrosion is primarily due to leaching of iron, zinc and copper from the corroding pipes into the treated water. Although these metals are all essential for both plant and animal life processes (75), their presence in water in excess of
the maximum contaminant levels (MCL) causes a number of problems such as the discoloration of water, taste and odor, and staining of laundry and fixtures (76). The presence of iron in drinking water causes red water complaints, increases turbidity, stimulates growth of iron bacteria and aids in the formation of deposits (77). The addition of zinc to water via the corrosive action of water on galvanized pipes imparts a bitter astringent taste to the water, leads to the growth of sand-like deposits and causes opalescence in water. Copper in potable water adds an unpleasant taste to the water. It causes discoloration and corrosion of pipe fittings and utensils (78). Wagner (26) reports that blue-green staining of fixtures may take place at copper concentrations of 0.5 mg/l or less. Corrosion of steel and cast iron may also add manganese to the water which causes black staining of fixtures. The secondary MCL value for Mn in water is 0.05 mg/l.

**Occurrence of Corrosive Waters**

The term corrosive waters is somewhat vague and may be misleading, for there are no natural waters that are absolutely noncorrosive to most engineering materials. One way to classify waters is by their hardness. Although it is generally believed that soft waters are more corrosive than hard waters, this assumption may not hold true if one considers the diverse group of structural materials used for conveying waters. Corrosive waters are typically low in total mineral content, alkalinity and pH.

The hardness of untreated public water supplies in the U.S. is quite variable from one section of the country to another (Fig. 1).
Waters of low hardness generally occur along the east coast and in the southeast and northwest regions of the country (16), indicating that a large portion of the population is exposed to potentially aggressive waters. Hudson and Gilcreas, in 1976, estimated that about 50 percent of the 100 largest cities in the U.S. were distributing corrosive waters to their customers (53).

Fig. 1. Hardness of Public Water Supplies (16).

In a recent survey of water supplies by the Environmental Protection Agency (EPA) in 35 geographically distributed areas in the U.S. serving approximately one-fifth of the U.S. population, it was found out that almost 70 percent of the represented utilities had moderately to highly aggressive waters (1). The survey included 130 utilities that were selected by the Bureau of Census to be representative of the U.S. population (Fig. 2).
In a similar study conducted by the Midwest Research Institute (MRI), it was shown that approximately 16 percent of the water utilities surveyed distributed aggressive waters and about 52 percent distributed waters that were moderately corrosive (79). Some 388 water utilities in the U.S. were included in the MRI study, serving a population of 103.5 million people.

Fig. 2. Geographic Distribution of Primary Sampling Points (1).

The corrosivity of waters in most of these studies was determined by the Langelier Saturation Index (LSI) (80), and/or the Aggressiveness Index (AI) (1). These studies clearly point out that the occurrence and distribution of corrosive waters in the U.S. is a widespread problem. In spite of the distribution of large quantities of corrosive
waters, it is surprising that very few utilities have implemented routine corrosion control programs. Available data indicate that only 500 of the 60,000 public water supplies in the U.S. (less than one percent) have adopted some procedures to combat corrosion (81).

Piping Materials

A water supply system is complex. The complexity of the system is apparent from the great diversity in quality of drinking water and the use of different types of construction materials under variable environmental conditions. The materials that are most commonly used in water supply systems include cast iron, mild steel, concrete, asbestos cement, galvanized steel, copper and plastics. Materials that are less frequently used include lead, aluminum, brass, bronze and stainless steel.

Among these materials of construction, iron, steel, concrete and asbestos cement pipes are used for water mains, and the rest are employed in household plumbing, valves, pumps, meters and other pipe fittings. Although comprehensive data with regard to the use of various types of pipes in water supply systems are limited, Donaldson (1924) reported the relative use of service pipe materials (3). In one of the surveys covering 539 utilities, 48 percent of the systems were using lead pipes, 42 percent indicated the use of iron or steel pipes, 32 percent contained galvanized iron and 5.7 percent used cast iron pipes (3).

In a similar study of 42 cities, mostly in Massachusetts, 67 percent of the cities reported lead plumbing, 47 percent cast iron and
47 percent galvanized steel pipes (3). The life of the piping materials has been estimated to vary widely, depending on the quality of water, the type of material and the conditions of exposure.

The results of a 1960 national survey of water supply systems (82) with regard to the use of different piping materials are summarized in Table 2.

Table 2. Materials Used in Water Distribution Systems (82)

<table>
<thead>
<tr>
<th>Type of Pipe</th>
<th>Percentage of Total Length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Distribution Mains Utility Lines</td>
</tr>
<tr>
<td>Cast Iron, unlined</td>
<td>53</td>
</tr>
<tr>
<td>Cast Iron, Cement Lined</td>
<td>28</td>
</tr>
<tr>
<td>Steel</td>
<td>9</td>
</tr>
<tr>
<td>Asbestos Cement</td>
<td>7</td>
</tr>
<tr>
<td>Concrete</td>
<td>2</td>
</tr>
<tr>
<td>Copper</td>
<td>-</td>
</tr>
<tr>
<td>Galvanized Iron</td>
<td>-</td>
</tr>
<tr>
<td>Brass, Lead, Plastic</td>
<td>-</td>
</tr>
<tr>
<td>Other</td>
<td>1</td>
</tr>
</tbody>
</table>

As indicated in Table 2, cast iron is the major component of most water distribution systems. The survey showed that about two-thirds of the cast iron pipes had not been lined with cement and therefore, are subject to direct corrosion attack. Steel mains have been in use for many years in water works, and those lined with epoxy have shown good resistance against corrosion (83). Asbestos cement pipe, especially those constructed after 1940, appears to offer satisfactory service in most stable waters. However, it has been
shown to be vulnerable to very soft waters (84).

Prestressed reinforced concrete has been a significant material of construction for water mains. Its use however is not recommended for waters of low mineral content which may leach calcium or alkalinity from cement or cement mortar (84-86).

The household plumbing or utility lines were shown (Table 2) to be primarily constructed of copper and galvanized iron. The wastewater piping inside the housing consisted mainly of copper, brass, steel, iron, lead and plastic (82).

A number of plastic pipes have been shown to possess desirable corrosion resistant qualities and have been used successfully for utility lines. These include PVC (polyvinyl chloride) (87); ABS (acrylonitrile-butadiene-styrene) (88); RPM (reinforced plastic mortar) (89); PB (polybutylene) (88); and PE (polyethylene) (90). The type and grade of plastic employed should bear the approval of the National Sanitation Foundation for satisfactory use. The use of unapproved plastics may add undesirable contaminants such as lead, cadmium, phenolic compounds and other chemicals (91).

It has been estimated that about 70 percent of the total water works capital is invested in distribution systems (82). The protection of this investment from corrosion and deterioration is of major interest both to the water utility and the scientific community.

**Regulatory Requirements**

The Safe Drinking Water Act, Public Law 93-523, was adopted by the U.S. Congress on December 16, 1974 (92). As a result of this law, the federal government, through EPA, established national drinking water
standards to ensure the safety of our drinking waters for the protection of public health. On March 14, 1975, EPA proposed the National Interim Primary Drinking Water Regulations (NIPDWR) which established maximum contaminant levels (MCL) for a number of chemicals including lead and cadmium (93). The primary regulations required that the MCL values be met at the consumer's tap. The NIPDWR were revised in December 1975 and went into effect on June 24, 1977.

On March 31, 1977, EPA proposed the National Secondary Drinking Water Regulations (NSDWR) which provided guidelines for those contaminants that are not harmful to health at the proposed levels, but are important as they affect the aesthetic quality of the water (94). As a result of NSDWR, the MCL values for iron, copper and zinc were established. The secondary regulations were promulgated on July 19, 1979 (95). The primary and secondary regulations for corrosion related contaminants are reported in Table 3.

Table 3. Corrosion By-Products Regulations (93, 94)

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>MCL</th>
<th>Regulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead (Pb)</td>
<td>0.05</td>
<td>primary</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>0.010</td>
<td>primary</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.30</td>
<td>secondary</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>1.0</td>
<td>secondary</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>5.0</td>
<td>secondary</td>
</tr>
<tr>
<td>Corrosivity</td>
<td>Non-Corrosive</td>
<td>secondary</td>
</tr>
</tbody>
</table>

It is important to note that some difficulty exists in defining "safe" levels for elements such as cadmium and lead in water. The
Commission of European Communities, for example, has proposed a 0.005 mg/l standard for cadmium in water (30). The National Academy of Sciences has recommended lowering the lead standard to 0.025 mg/l (24, 25).

The primary regulations supersede the U.S. Public Health Service drinking water standards of 1962. The NIPDWR further required that the primary contaminants be monitored once a year for surface sources and once every three years for ground water sources. However, it was felt by concerned parties that the required monitoring would not be adequate to detect the contamination of water by corrosion by-products in potentially aggressive water systems. Such systems would require a more frequent monitoring. As a result of this, EPA, on July 19, 1979, proposed an amendment to the NIPDWR which included requirements for community water supplies that distribute corrosive water to carry out a corrosion control program (96). The proposed amendments to NIPDWR for corrosion control calls for the initiation of surveys to identify the presence and source of corrosion products and the implementation of an appropriate corrosion control program by the state.

**Objective of Study**

With the passage of Safe Drinking Water Act, the primary and secondary regulations and finally the amendments of primary regulations for corrosion control, the challenge and responsibility of the water utility and the research community becomes greater than ever. The magnitude and extent of the problem is clear from the above discussion.
No general rule exists for identifying and measuring corrosion in domestic waters. Many corrosion indices have been developed in the past and new improvements have been introduced to these models by several investigators. In spite of these refinements, it is well understood that under many conditions these indices have failed to define accurately the aggressiveness of given waters. These anomalies are not just chance phenomena, but occur due to some inherent deficiencies in the development and formulation of the corrosion indices. For example, the Langelier Saturation Index, LSI (80), Ryznar Index, RI (97), McCauley's Driving Force Index (98), Dye Momentary Excess (99) and Aggressiveness Index, AI (1) are all based on the theoretical saturation of water with respect to CaCO$_3$, and do not take into account the effect of many major cations and anions as well as the presence of various gases. Most of the water quality parameters play important roles in corrosion reactions. Riddick's Corrosion Index (100), although not enjoying as much popularity as some of the other indices, none the less, did include several important parameters such as dissolved oxygen, chloride, nitrate, silicate, as well as carbon dioxide, hardness and alkalinity. These above stated inconsistencies clearly point out to a genuine need for some basic research on corrosion of potable waters. A universal corrosion index will only be useful as a true indicator of corrosivity of a given water if the various water quality parameters contributing to the aggressiveness of water are incorporated in such a model.

This study was designed to investigate the effect of various water quality parameters on the rates of corrosion of several important
metals such as mild steel, galvanized steel and copper. More specifically the effects of major cations such as Ca\(^{++}\), Mg\(^{++}\), Na\(^{+}\) and major anions such as Cl\(^{-}\), SO\(_4^{2-}\) and HCO\(_3^{-}\) as well as the effects of pH, dissolved oxygen, chlorine residual and natural color will be evaluated. While the writer acknowledges the difficulty of conducting a comprehensive corrosion research program that would lead to the development of a universal corrosion index, in light of the limited time and resources available for this task, he is certain that the findings of this research will serve as a first step toward the formulation of such a highly needed index.
CHAPTER II
LITERATURE REVIEW

Definition of Corrosion

The word "corrosion" originates from the Latin word corrodere which means to "gnaw away" (101). Webster defines corrosion as "the action or process of corrosive chemical change . . . a gradual wearing away or alteration by a chemical or electrochemical essentially oxidizing process as in the atmospheric rusting of iron" (102:512).

Corrosion, then, is the destruction of a material by a chemical or electrochemical reaction with the environment. This is a broad definition and includes both metals and non-metals. However in potable water supplies, there is concern primarily with metallic corrosion. Metallic corrosion employs the disintegration or conversion of a metal to a metallic oxide or compound which some authors call "extractive metallurgy in reverse" (4:2). For a typical metal such as iron, the simplified extraction and corrosion processes are illustrated in equations 1 (extraction) and 2 (corrosion) respectively.

FeO, Fe₂O₃
FeS, Fe₃O₄ + Energy = Elemental + Impurities (1)
Heat Fe O₂, S, C
Elements of the Metallic Compound
Environment FeO, Fe₂O₃, FeS, + Energy (2)
H₂O, O₂, S, CO₃, etc.
e etc.

Metals are extracted from their ores because they possess many valuable engineering properties that are otherwise absent in their
metallic compounds. The various metallurgical processes used for the extraction of metals from their native ores are endothermic (103). This means that large quantities of energy have to be supplied in the form of heat (equation 1) during the conversion process. Since metals contain more free energy than their corresponding native compounds, there is a natural tendency for the metals to corrode or revert to their stable forms. Thus energetically all metallurgically extracted metals are subject to corrosion when exposed to the elements of the environment.

Principles of Corrosion

From the definition of corrosion, it is clear that corrosion of metals is an electrochemical phenomenon, meaning that chemical reactions occur in such systems through the transfer of electrons. It should be pointed out that not all corrosion reactions are electrochemical. The dissolution of calcium carbonate by an aggressive water is an example of a chemical corrosion in which no electrons are involved. However, most corrosion reactions are electrochemical in nature. According to Faraday's Law, the rate of corrosion is directly proportional to the flow of current in an electrochemical reaction (104).

\[
\text{mpy} = \frac{0.13 \text{ Ie}}{\text{D}}
\]

where mpy is corrosion rate in mils per year; I is current density in microamp./sq. cm.; e is equivalent weight of the metal in grams; and D is density of metal in g./cu. cm.

Free Energy and Electrode Potentials

The tendency of a metal to undergo change from the metallic to ionic form is quite different for different metals. This tendency, as
for any reaction, is measured by the Gibbs free energy change, $\Delta G$. The change in Free energy is defined as (105):

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (4)

where $H$ is the change in heat content or enthalpy, $T$ is the absolute temperature and $\Delta S$ is the change in entropy. The change in free energy is a measure of the spontaneity of a reaction toward equilibrium. At equilibrium, the change in free energy is zero.

$$A_{\text{ox}} + ne = A_{\text{red}}$$  \hspace{1cm} (5)

For the reaction shown in equation 5, (106), the actual change in free energy $\Delta G$, is a function of both standard free energy, $\Delta G^0$, and of the reacting redox species (107) as shown in equation 6.

$$\Delta G = \Delta G^0 - 2.3 \text{ RT} \log \frac{A_{\text{ox}}}{A_{\text{red}}}$$  \hspace{1cm} (6)

The more negative the value of $\Delta G$, the greater is the tendency for the reaction to proceed in the direction written. Consider the standard free energies (Table 4) for the following reactions (108).

The values of $\Delta G^0$ indicate that reactions 7–9 will occur spontaneously as written, while reaction 10 will have a very low tendency to form $\text{Au(OH)}_3$.

Corrosion in addition to being electrochemical, is a surface phenomenon. When corrosion occurs, atoms of metal leave the surface of the metal and enter the solution as positive ions, leaving behind a number of excess electrons. The site at which this oxidation reaction occurs is known as the "anode." In the case of dissolution of iron, the reaction can be written as seen in Table 4.
Table 4. Standard Free Energies, $\Delta G^0$, for Some Reactions (108)

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>$\Delta G^0$, K Cal Mole</th>
<th>Eq. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca + $H_2O + \frac{1}{2} O_2 = Ca(OH)_2$</td>
<td>-157.53</td>
<td>(7)</td>
</tr>
<tr>
<td>Fe + $H_2O + \frac{1}{2} O_2 = Fe(OH)_2$</td>
<td>- 58.88</td>
<td>(8)</td>
</tr>
<tr>
<td>Cu + $H_2O + \frac{1}{2} O_2 = Cu(OH)_2$</td>
<td>- 28.00</td>
<td>(9)</td>
</tr>
<tr>
<td>Au + $3/2 H_2O + 3/4 O_2 = Au(OH)_3$</td>
<td>+ 15.74</td>
<td>(10)</td>
</tr>
<tr>
<td>Fe = Fe$^{++} + 2e^-$ anodic (oxidation reaction)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

At the same time, the free electrons produced in the anodic reaction travel through the metal under the influence of a potential difference to another location known as the "cathode", and there react with ions or atoms which are present in the solution. In oxygen saturated potable waters, in near neutral pH conditions, the predominant cathodic reaction is the reduction of oxygen to hydroxyl ions.

$$2 \text{H}_2\text{O} + \text{O}_2 + 4 \text{e}^- = 4\text{OH}^- \text{ cathodic (reduction reaction)} \quad (12)$$

The circuit between the anode and cathode is completed by the movement of ions in the solution. Reactions 11 and 12 of the corrosion of ion in an aerated water are shown in Fig. 3. In order to preserve electroneutrality of the system, the anodic or cathodic reaction must occur simultaneously and at the same rate.

Corrosion can also be explained by the Ohms Law (104, 108). A metal surface due to the presence of impurities is composed of many microcells of different potentials that are connected to each other by the metal itself.
Ohms Law,

\[ I = \frac{\Delta E}{R} \]  \hspace{1cm} (13)

states that the total current carried by electrons in a metallic conductor upon short-circuiting, equals the quotient \( \Delta E/R \), where

\[ \Delta E \text{ is the potential difference in volts and } R \text{ is the total resistance in the metallic circuit in ohms. Without the presence of an electrolyte, no corrosion occurs. The current that flows in the metal is lost in heating the metal through which it flows. If an electrolyte is present, corrosion of metal takes place due to the flow of the current by the ions in the electrolyte. In other words the total flow} \]
of current in the metallic path is exactly equal to the total flow of the current in the electrolyte (108).

In view of the electrochemical mechanism of corrosion, the tendency of metals to corrode can be expressed quantitatively as the electrode or reduction potential when the reaction is written as (106):

\[ M^{n+} + ne = M \quad \text{E}^0 \text{ (volts)} \quad (14) \]

The standard electrode potential, E\(^0\), in volts, shown for the reaction is the reduction potential of the substance when in contact with an aqueous solution of its ions at unit activity at 25\(^\circ\) C. The electrode potentials are measured against an arbitrary selected reference reaction called the "normal hydrogen electrode", NHE.

\[ 2\text{H}^+ \text{(1 N)} + 2e = \text{H}_2 \text{(g) (1 atm.)} \quad \text{E} = 0.000 \text{ volts} \quad (15) \]

It is not possible to make an electrode from hydrogen gas, an inert electrode such as platinum is used to establish a reversible hydrogen electrode. Corrosion cell potentials can be computed easily from the half-cell potentials of the anode and the cathode involved in the overall reaction. The larger or more positive the value of the electrode potential, the less active or more noble is the metal. The standard EMF series gives the electrode potentials of different metals under standard conditions. The electrode potentials in other than standard conditions are affected by many factors including the metal ion concentration, the purity of the metal, the presence of other ions in the electrolyte, and the flow of current and temperature (109).

The electrode potential increases (becomes more noble) with increasing metal ion concentration in the electrolyte. In other words
a metal would tend to enter an electrolyte devoid of its own ions. Due to the limitations of the EMF series, the galvanic series of metals and alloys is a more practical way of presenting their measured potentials in a non-standard environment of exposure (108).

Electrode potentials and free energies are related according to the following equation:

\[ \Delta G^0 = -nF\Delta E^0 \]  
(16)

with \( n \) being the number of electrons involved in the reaction and \( F \) is the Faraday (96500 coulombs/equivalent), \( \Delta G^0 \) and \( \Delta E^0 \) are the change in free energy and electrode potential at standard states respectively. If the redox components are not at their standard states, then

\[ \Delta G = -nF\Delta E \]  
(17)

The electrode potentials at different concentrations of soluble redox species are calculated with the aid of the Nernst equation (106, 110). Considering the half reaction of equation 5,

\[ A_{\text{ox}} + ne = A_{\text{red}} \]  
(5)

The equilibrium constant, \( K \) for this reaction is:

\[ K = \frac{A_{\text{red}}}{A_{\text{ox}}} \]  
(18)

The Nernst equation is:

\[ E = E^0 + 2.303 \frac{RT}{nF} \log \frac{A_{\text{ox}}}{A_{\text{red}}} \]  
(19)
where $E$ = the potential in volts

$E^\circ$ = the standard electrode potential in volts

$R$ = the gas constant (8.314 Joules/deg. mole)

$T$ = the Absolute temperature, °K (273 + Temp. °C)

$n$ = the number of electrons involved in the reaction

$F$ = the Faraday (96500 coulombs/equivalent)

$A_{\text{ox}}$ = the activity of the oxidized form

$A_{\text{red}}$ = the activity of the reduced form

In dilute aqueous solutions, the activities are essentially the same as molar concentrations. At room temperature, 25°C (298°K) the Nernst equation has the following simple form:

$$E = E^\circ + \frac{0.059}{n} \log \frac{A_{\text{ox}}}{A_{\text{red}}} \quad (20)$$

The actual potential of an electrode (Eq. 20) depends on the ratio of the oxidized to reduced species in the solution. In half reactions that involve hydrogen ions, the hydrogen ion concentration is included in the Nernst equation. At equilibrium ($E = 0$), equation 20 becomes:

$$E^\circ = 0.059 \frac{n}{n} \log \frac{A_{\text{ox}}}{A_{\text{red}}} \quad (21)$$

Alternatively,

$$E^\circ = -\frac{0.059}{n} \log \frac{1}{k} = \frac{0.059 \log k}{n} \quad (22)$$

substituting $E^\circ$ in equation 16, the relation between the standard free energy and the equilibrium constant is obtained:

$$\Delta G^\circ = -2.3 RT \log K \quad (23)$$

A summary of the relationships between Gibbs free energy, $\Delta G$, and
redox potential, \( E \) for a reaction is presented in Table 5.

<table>
<thead>
<tr>
<th>Reaction as Written</th>
<th>( \Delta G )</th>
<th>( E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spontaneous</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>No tendency to occur</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Several conditions have to be met for the corrosion of metals to take place: the presence of anodic and cathodic sites on the metal surface, the presence of an electrolyte (water or moisture containing ions) and electrical conductors which provide the electrical continuity between the anodic and cathodic sites. All that is required for the initiation and propagation of corrosion is the presence of an electrolyte. Drinking waters are dilute electrolyte systems containing variable concentrations of many inorganic and organic substances, depending on the hydrogeological sources of the waters and the treatment. For a better understanding of the process of corrosion in drinking waters, the chemistry of the normal components of a potable water is briefly discussed.

**Chemical Composition of Water**

Fresh waters as opposed to sea water are more variable in composition depending on their source and type of treatment. Almost all waters contain variable concentrations of the following major cations and anions in addition to other impurities. The major ions include \( \text{Ca}^{++}, \text{Mg}^{++}, \text{Na}^{+}, \text{HCO}_3^-, \text{SO}_4^{2-} \) and \( \text{Cl}^- \).
Major cations

Calcium. Calcium, which stands fifth in the order of abundance in earth's crust (3.4%), is present in most water supplies (111). The presence of calcium in water results from passage or contact of water with limestone (CaCO$_3$), gypsum (CaSO$_4$), sandstone and gypsisiferous shale (107). Calcium is easily dissolved by acid (CO$_2$) bearing waters. The solubility of calcium in water is pH dependent, and its precipitation is controlled by the carbonate ion concentration.

$$
Ca^{++} + CO_3^{=} = CaCO_3 \quad k_{sp} = 5.0 \times 10^{-9} \text{ at } 25^0 C \tag{24}
$$

Calcium forms complexes with ligands, the net effect of which is the reduction of the free ion concentration in water. Calcium is an essential element for all organisms. There is no public health limit for calcium. Its possible role in cardiovascular diseases was discussed earlier. High Ca is undesirable in that as a component of hardness, it causes soap precipitation and harmful scaling in boilers and hot water pipes. The concentration of calcium may range from zero to several hundred mg/l.

Magnesium. Magnesium ranks eighth among the elements in order of abundance (1.9%) and is a common constituent of water supplies (111). Magnesium sources are carbonate rocks, magnesium silicate rocks and dolomite. Magnesium tends to remain in solution more than calcium. Magnesium solubility is controlled more by (OH$^-$) than by carbonate (CO$_3^{=}$. At magnesium levels of natural waters, precipitation of Mg(OH)$_2$ can occur above pH 9.5-10.5. The concentration of Mg in fresh waters is generally less than or perhaps equal to that of calcium. Calcium is
more abundant in sedimentary rocks than Mg and hence tends to be more abundant in fresh waters. Magnesium is an important component of hardness and forms objectionable scale in boilers. There is no public health limit for magnesium in drinking waters (107).

**Sodium.** Sodium ranks sixth among the elements in order of abundance in the earth's crust (111). It is therefore present in most natural waters. The concentration of sodium may vary from a few ppm to relatively high concentrations in brines and hard waters softened by the sodium ion exchange process. In most drinking waters it rarely exceeds 100 ppm. All simple salts of Na are quite soluble and sodium is present as Na\(^+\) in water. The major sources of sodium are from weathering of rocks and soils, marine evaporates, irrigation and oilfields, meat packing (107) and water treatment (ion exchange process). There is at present no public health limit for Na in water, although it is an important element in both agriculture and in human pathology. Sodium may have possible effect on cardiovascular diseases (111).

**Alkalinity and the carbonate system**

The chemistry of water is influenced by the ability of water to dissociate to H\(^+\) and OH\(^-\) ions, as shown in the following reaction (112).

\[
H_2O = H^+ + OH^- \quad (25)
\]

Although a very small fraction of water ionizes to form hydrogen and hydroxyl ions (about \(10^{-7}\) M H\(^+\) and OH\(^-\) at room temperature at equilibrium), this gives water the ability to take part in many reactions.
The alkalinity of an aqueous solution is defined as its acid neutralizing capacity (111, 112, 113). Alkalinity is usually imparted by the bicarbonate \( \text{HCO}_3^- \), carbonate \( \text{CO}_3^{2-} \) and hydroxide \( \text{OH}^- \) components of a water. The capacity of water to resist changes in pH is termed its buffer intensity. The alkalinity of a water buffered by the carbonate system is mathematically defined by the following charge balance equation:

\[
\text{Total Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (26)
\]

Since most natural waters have pH values between 6 and 9, the last two terms in equation 26 cancel each other at neutral or near neutral pH conditions. Furthermore, since the predominant chemical species in the carbonate system in this pH range is \( \text{HCO}_3^- \), the alkalinity of water essentially is equivalent to the amount of bicarbonate present in the solution (Eq. 26).

**Sulfate.** Sulfate is widely distributed in nature and its concentration in water may range from a few to several thousand mg/l. The primary sources of \( \text{SO}_4^{2-} \) include weathering of \( \text{CaSO}_4 \) and many pyrite and sulfide minerals. Additional sources are from burning of coal and decay of organic matter. The most important reactions for \( \text{SO}_4^{2-} \) in the sulfur cycle are redox reactions. Sulfate reduction to sulfide \( (\text{SO}_4^{2-} \rightarrow \text{S}^-) \) occurs under anaerobic conditions and is mediated by sulfur bacteria. Sulfate is used as the terminal electron acceptor in place of oxygen. Elemental sulfur is present in sulfur bacteria, but intermediate oxidation states such as sulfite \( (\text{SO}_3^{2-}) \), and thiosulfate \( (\text{S}_2\text{O}_3^{2-}) \) are thermodynamically unstable in natural waters (107).
Oxidation of sulfide to $\text{SO}_4^-$ is a complex biological reaction carried out by some bacteria. Sulfur is a biogenic element, present in proteins as the SH (sulfhydryl) group. The recommended public health limit for $\text{SO}_4^-$ in drinking water because of taste is 250 ppm.

Anoxic waters containing high $\text{SO}_4^-$ can lead to odor problems due to reduction of $\text{SO}_4^-$ to hydrogen sulfide ($\text{H}_2\text{S}$). Hydrogen sulfide is a weak acid, $\text{pK}_1 = 7.0$, $\text{pK}_2 = 12.9$. Most metal sulfates are soluble, while sulfides of heavy metals (FeS, MnS, CdS and PbS) are very insoluble (107, 111).

**Chloride.** Chloride is a nonbiogenic element and is one of the major anions in water. The sources of chloride include brine, food processing, salt on streets, domestic consumption and NaCl regenerant of softening resins. High Cl$^-$ content, aside from a salty taste exerts a deleterious effect on metallic structures as well as agricultural plants. Chloride has a simple chemistry. Other oxidation states of chloride are not found in natural waters, but chlorine and salts of HOCL are used as disinfectants in drinking waters. The public health limit for chloride is set at 250 ppm for taste problems (111).

Although most drinking waters contain the major cations and anions mentioned earlier, other constituents may also be present in certain waters. These include dissolved oxygen, carbon dioxide, $\text{H}_2\text{S}$, color, trace metals, fluoride, potassium, bacteria and other biological organisms, chlorine, silica and organic matter (107).

**Anodic and Cathodic Reactions**

The presence of major cations and anions in the water, along with other impurities, results in the possibility of many anodic and
cathodic reactions. Some of the most common reactions in the corrosion of iron in water are as follows (81, 114, 115):

\[ \text{Fe} = \text{Fe}^{++} + 2\bar{e} \]  
(27)

\[ \text{Fe} + \text{CO}_3^{-} = \text{FeCO}_3 + 2\bar{e} \]  
(28)

\[ \text{Fe} + 2\text{OH}^- = \text{Fe(OH)}_2 + 2\bar{e} \]  
(29)

\[ 2\text{Fe (OH)}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = 2\text{Fe (OH)}_3 \]  
(30)

\[ \text{Fe} + 2\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 = \text{Fe(OH)}_3 + \text{H}^+ + \bar{e} \]  
(31)

\[ \text{H}_2\text{O} = \text{H}^+ + \text{OH}^- \]  
(32)

\[ \text{Fe} + \text{HSiO}_3^- = \text{FeSiO}_3 + \text{H}^+ + 2\bar{e} \]  
(33)

\[ \text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^- \]  
(34)

\[ \text{HCO}_3^- = \text{H}^+ + \text{CO}_3^- \]  
(35)

\[ \text{H}_2\text{S} + \text{H}^+ + \text{HS}^- \]  
(36)

\[ \text{HS} = \text{H}^+ + \text{S}^- \]  
(37)

\[ \text{Cl}_2 + \text{H}_2\text{O} = \text{H}^+ + \text{Cl}^- + \text{HOCl} \]  
(38)

\[ \text{HOCl} = \text{H}^+ + \text{OCl}^- \]  
(39)

\[ \text{Cl}_2 + \text{H}_2\text{S} = 2\text{H}^+ + 2\text{Cl}^- + \text{S} \]  
(40)

\[ 4\text{Cl}_2 + \text{H}_2\text{S} + 4\text{H}_2\text{O} = 10 \text{H}^+ + 8\text{Cl}^- + \text{SO}_4^- \]  
(41)

\[ \text{H}_2\text{O} + 2 \bar{e} + \frac{1}{2}\text{O}_2 = 2\text{OH}^- \]  
(42)

\[ \text{Fe}^{+++} + \bar{e} = \text{Fe}^{++} \]  
(43)

\[ \text{Fe}^{++} + 2\text{H}_2\text{O} = \text{Fe(OH)}_2 + 2\text{H}^+ \]  
(44)

\[ 2\text{Fe}^{++} + 5\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 = 2\text{Fe(OH)}_3 + 4\text{H}^+ \]  
(45)

\[ 2\text{FeCl}_2 + 5\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 = 2\text{Fe(OH)}_3 + 4\text{HCl} \]  
(46)

\[ 2\text{FeSO}_4 + 5\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 = 2\text{Fe(OH)}_3 + 2\text{H}_2\text{SO}_4 \]  
(47)
$2\text{Fe(HCO}_3\text{)}_2 + 5\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 = 2\text{Fe(OH)}_3 + 4\text{H}_2\text{CO}_3 \quad (48)$

$2\text{Na}^+ + 2\text{H}_2\text{O} + 2\bar{e} = 2\text{NaOH} + \text{H}_2 \quad (49)$

$\text{Ca(OH)}_2 + \text{Ca(HCO}_3\text{)}_2 = 2\text{CaCO}_3 + 2\text{H}_2\text{O} \quad (50)$

From equations 27-50, it is evident that some reactions involve iron or its compounds while others do not. These reactions that do not include iron are necessary to provide the major constituents for the progress of corrosion reactions. For metals other than iron, most of these chemical reactions exert more or less the same effects.

Each of these reactions have electrode potentials that are different from one another. In corrosion reactions, where several anodic and cathodic reactions are possible, those with the highest and the lowest potentials will dominate.

**Pourbaix Diagrams**

One of the most important contributions to corrosion literature has been the work of Pourbaix and associates in the development of thermodynamic equilibrium diagrams (116) ($E_H$ vs pH) for the behavior of metals in aqueous environments. The construction of such diagrams is useful in understanding corrosion processes in potable waters. They show the conditions of thermodynamic stability of metals and their compounds and define theoretical conditions for corrosion, immunity and passivation. Pourbaix diagrams have been constructed for iron, copper and zinc in aqueous solutions containing $10^{-3} \text{ M} (100 \text{ mg/l})$ alkalinity, as CaCO$_3$, and a total metal ion concentration equal to the specified maximum contaminant level.

These diagrams are shown in the next three figures for the pH range of 4-12, the range of concern in potable water systems. In construction
of the Pourbaix diagram for the Fe - H₂O - Alkalinity system at a
temperature of 25°C, the following chemical species were considered
(Fig. 4): Fe, Fe₂O₃, Fe₃O₄, Fe(OH)₂, Fe(OH)₃, FeCO₃, Fe⁺⁺⁺, Fe(OH)⁺⁺
and Fe(OH)⁺.

Fig. 4 was constructed for a metal ion concentration of 5 x 10⁻⁶
moles per liter equal to 0.3 mg/l Fe, and an alkalinity of 100 mg/l,
as CaCO₃. The area between the two dashed parallel lines is the
region of thermodynamic stability of water under atmospheric pressure.
At the upper line water is in equilibrium with oxygen, above which
water is oxidized to oxygen. The lower line of water stability defines
the coexistence of water and hydrogen, below this line water is reduced
to hydrogen (116).

The regions of stability or the areas of predominance of the stable
species under the specified conditions are defined by the lines indicated.
The stable species may be the metal itself, the solid oxide, or any
other insoluble product, or the dissolved species.

The iron diagram shows that metallic iron, Fe, and water are not
stable simultaneously, because the area of predominance of Fe falls
below the region of stability of the water.

Pourbaix diagram of copper, constructed for 1.6 x 10⁻⁵ moles per
liter (1.0 mg/l Cu), in an aqueous solution containing 100 mg/l alka-
linity, as CaCO₃, at a temperature of 25°C is shown in Fig. 5. The
species considered for the construction of this diagram included Cu,
CuO, Cu₂O, Cu(OH)₂, Cu₂(OH)₂CO₃, Cu₃(OH)₂(CO₃)₂, CuCO₃, Cu⁺, Cu⁺⁺,
HCuO₂⁻, CuO₂⁻ and Cu(CO₃)²⁻.
Fig. 4 Pourbaix Diagram for $5 \times 10^{-6}$ M Fe in the presence of 100 mg/l Alkalinity as CaCO$_3$. 
Fig. 5. Pourbaix Diagram for 1.6 x 10^{-5} M Cu in the presence of 100 mg/l Alkalinity as CaCO₃.

Electrode Potential,  E^H_° Volts
It is seen from Fig. 5 that of all the species considered, only Cu, Cu$_3$(OH)$_2$(CO$_3$)$_2$, Cu$_2$O, CuO, and Cu(OH)$_2$ are stable forms of copper under the defined conditions. Considering only the dissolved species, Cu$^+$, Cu$^{++}$, Cu(CO$_3$)$_2$ and HCuO$_2^-$ are the predominant species as shown by the dotted lines.

It is interesting to note that in contrast to iron, metallic copper, Cu, is stable within certain regions of the stability of water. This property makes copper a more useful material of construction for water supply systems. In other words, if the redox potential of the solution is below the Cu-Cu$_2$O line, copper will not corrode.

Fig. 6 is a Pourbaix diagram of zinc constructed for 7.6 x 10$^{-5}$ moles per liter of zinc ions, equal to 5 mg/l Zn, in an aqueous solution containing 100 mg/l of alkalinity, as CaCO$_3$, at a temperature of 25°C. The species considered were Zn, ZnO, Zn(OH)$_2$, ZnCO$_3$, Zn$^{++}$, Zn(OH)$^+$ and ZnO$_2^-$ . Of all the species considered, only Zn$^{++}$ and ZnO are stable as can be seen from Fig. 6. Metallic zinc, Zn, is unstable in water because its region of stability is well below the stability area of water in the Pourbaix diagram. Fig. 6 further indicates that zinc in contact with water exists as Zn$^{++}$ below pH 7.52 and as ZnO above a pH value of 7.52. In other words, zinc will corrode or oxidize readily below the neutral pH of water as presented in Fig. 6.

It should be noted that a computer program developed at the University of Florida (117) was employed in the calculation of the equilibrium equations and the construction of the Pourbaix diagrams. The computer program uses thermodynamic data for balancing chemical equilibrium equations by applying the Nernst equation (118).
Fig. 6. Pourbaix Diagram for 7.6 x 10^{-5} M Zn in the Presence of 100 mg/l Alkalinity as CaCO_3.
This approach is based solely on the thermodynamics of the reactions and hence cannot predict the rates of the reactions. It provides useful information as to the feasibility of a reaction and aids in understanding the chemistry of corrosion processes. It should also be pointed out only metal-water-alkalinity systems were considered here. The presence of chloride or sulfate ions and oxidizing or reducing agents all would influence the electrode potentials and hence alter the areas of predominance and the stability of various species in Pourbaix diagrams.

Since the major concern is the rates of corrosion of metals in aqueous solutions rather than the thermodynamics of corrosion, the former will be investigated over a wide range of actual service conditions.

**Polarization and Passivity**

As pointed out earlier, corrosion of a single metal in an aqueous solution involves the flow of current from anodic sites to cathodic sites on the metal surface (Fig. 3). This flow of current changes the electrode potentials of both anode and cathode from their equilibrium values. The change in electrode potential due to passage of current in a corroding system is called polarization (119). Up till now the main focus of this review was on the application of thermodynamic and equilibrium principles to study electrochemical reactions. However, corroding systems are dynamic systems and equilibrium conditions do not describe the rates of corrosion reactions. The measurement of polarization is an important parameter in corrosion studies. Polarization is normally measured in terms of overvoltage (4) with respect
to equilibrium potential of an electrode that is taken as a zero reference.

Polarization of electrodes in an aqueous solution is caused by the accumulation of corrosion products, the formation of a film of oxide or gas on the surface of electrodes. It is generally caused by some slow reaction at the electrode surface (such as the slow movement of corroded metal ions from the metal surface to the bulk of the solution), electron transfer and slow combination reactions (119). These changes in potential, reduce the potential difference between the anode and the cathode areas from their equilibrium open circuit (zero-current) potentials.

During polarization, the potentials of each electrode approach each other as the current increases. A typical polarization curve for the corrosion of iron in an acid solution is shown in Fig. 7 (104, 119).

When no current is flowing between the anode and the cathode, say due to an infinite or large electrical resistance between the anode and the cathode in the solution, according to Ohms Law (Eq. 13), no corrosion would occur and the electrode potentials will remain at their open-circuit potentials, \( E_a \) and \( E_c \). On the other hand, if the resistance were zero or very small, the current will approach infinity resulting in a strong and active corrosion.

When the resistance of the circuit (metal, electrolyte, surface films) is decreased to a certain value, a current \( I_1 \) will flow which will polarize the anode in the cathodic direction and the cathode in the anodic direction. If the resistance were lowered further, a
higher current $I_2$ will flow between the cathode and the anode causing further polarization of the electrodes. Since the resistance of the metallic path between the anode and the cathode is quite small due to their close spacing on the metal surface, the IR drop is primarily due to the resistance of the electrolyte.

In addition, during corrosion, the difference between the potentials of the polarized electrodes must be small to satisfy equation 13 for the flow of a maximum current $I_{\text{corr}}$ ($I_{\text{corr}}$).

$$I = \frac{\Delta E}{\varepsilon R}$$  \hspace{1cm} (13)
The point of intersection of the anodic and cathodic polarization curves (Fig. 7) for a freely corroding metal in an electrolyte, is an appropriate way of expressing the true corrosion conditions (104), although in reality the two curves never intersect as long as the metal is corroding. A freely corroding metal in an aqueous solution corrodes at a compromised potential $E_{\text{corr}}$, and a corrosion current density of $I_{\text{corr}}$ between the anode and the cathode areas. Thus corrosion potential is different than the previously discussed electrode potentials.

Polarization of the electrodes is greatly affected by current, electrode area, electrolyte movement, presence of polarizing and depolarizing substances and temperature.

Polarization curves are important in corrosion control process, because the rate of corrosion is influenced by polarization. As the degree of polarization of either anode or cathode is increased, the rate of corrosion is decreased. Polarization could be under cathodic control, anodic control, mixed control or resistance control depending on the degree of polarization of the cathode, anode or both (104,108). The effects of polarization and the types of control are presented in Fig. 8. When neither anode nor cathode are significantly polarized due to a high resistance in the electrolyte, the corrosion rate is said to be under resistance control. Polarization is under cathodic control if most polarization occurs in the cathode (Fig. 8 a), and $E_{\text{corr}}$ is near $E_a$. It was mentioned earlier that polarization occurs due to some slow reactions on the electrodes surfaces. These
Fig. 8. Types of Corrosion Control by Polarization (A) Cathodic Control (B) Anodic Control (C) Mixed Control (D) Resistance Control. H.P. - High polarization; L.P. - Low polarization.
slow reactions are basically due to activation, concentration, and IR drop. The slow step reaction of hydrogen evolution at the cathode which is controlled by the reaction sequence at the metal surface is called activation polarization. The hinderance of a reaction at an electrode surface which is controlled by the diffusion of ions or molecules in the electrolyte is called concentration polarization. For example, in case of hydrogen evolution, the diffusion of hydrogen ion is slower than its reduction reaction. The IR-drop is the drop in potential in any polarization reaction across the electrolyte and surface films on the electrodes (104).

The Tafel equation (4, 108) describes the relation between activation overvoltage and current density, $I$:

$$N_a = \frac{1}{\beta} \log \frac{I}{I_0}$$  \hspace{1cm} (51)

where $N_a$ is activation overvoltage, $\beta$ is the Tafel constant. $I_0$ is the exchange current density which is equal to the rate of oxidation-reduction reaction for an electrode at equilibrium (equal forward and reverse current with no net current flow). According to the Tafel relation, activation overvoltage is a linear function of current density if a logarithmic scale is used for the current density, $I$. (Fig. 9a).

Concentration polarization is described by the following equation (4), for a cathodic reaction:

$$N_c = 2.3 \frac{RT}{NF} \log \left(1 - \frac{I}{I_L}\right)$$  \hspace{1cm} (52)
Fig. 9. Types of Polarizations (A) Activation Polarization (B) Concentration Polarization (C) Activation plus Concentration Polarization.
where \( I_L = \frac{DnFC_b}{x} \)  

(53)

\( I_L \) is the limiting diffusion current sensitivity which is the maximum rate of reduction in a given system, \( n \) is the diffusion coefficient of the reacting ions, \( C_b \) is the concentration of the reacting ions in the bulk solution and \( x \) is the thickness of the diffusion layer (Fig. 9b).

The combined polarization for a reduction process is described by the sum of equations 51 and 52, (4) as follows:

\[
N = -\beta \log \frac{I}{I_o} + 2.3 \frac{RT}{NF} \log \left(1 - \frac{I}{I_L}\right)
\]

(54)

It should be noted out that the positive sign in equation 51 applies to all anodic dissolution reactions, while the negative sign is for cathodic processes (Fig. 9c). The two main types of polarization and their combination for a cathodic process are illustrated in Fig. 9. Increasing velocity decreases concentration polarization and hence increases the rate of corrosion, while it does not affect activation polarization significantly (120).

Passivity is an electrochemical quality exhibited by some metals and alloys in which they tend to behave as noble metals under certain conditions. A passive metal, although thermodynamically unstable, could act as an inert material in a particular electrolytic solution (4). Passivity is basically an anodic phenomenon, but it also depends on cathodic polarization. The electrode potential of a passive metal is normally more noble than its potential in the active state. Some metals capable of passivity include: iron, aluminum, lead, nickel, chromium, silicon and their alloys (3). Passivation is generally due
to the formation of thin (30 A°) protective oxide films on metal surfaces (121). Passivation may also occur due to the formation of a layer of corrosion products on the metal surface that inhibits further corrosion (122).

The subject of passivity has been covered in detail by several authorities on corrosion (121, 122, 123). A typical polarization curve for passive metals is shown in Fig. 10.

![Anodic Polarization Curve for a Passive Metal](image)

Fig. 10. Anodic Polarization Curve for a Passive Metal

When the potential for a passive metal or alloy is increased in the active direction (A to B), the current density increases until it reaches a critical current density, \( I_{\text{crit}} \) at point B. This is called the active polarization region in which the anodic polarization of a passive metal is like that of a non-passive metal. If the potential is increased further, the current density decreases until it reaches
a minimum value called the passive current density, I\text{pass}. (point C). This is the beginning of the passive state, and the metal will remain passive regardless of any further increase in potential until the potential coincides with point D. Beyond point D, an increase in potential will cause an increase in current density and the corrosion rate will increase. The regions between A and B is called active, and that between B and C is called transition, which is electrically unstable. The region between C and D is passive, while that beyond point D is termed transpassive (123).

The potentials that correspond to points B, C and D are called the primary passive potentials, Epp, Flade potential \( E_F \), and pitting potential \( E_P \) respectively. Passivation of an alloy in a given situation depends on both anodic and cathodic polarization curves. The effects of both anodic and cathodic polarization on passivity of metals are presented in Fig. 11. The rates of corrosion for the anodic polarization curves A and B are greatly affected by the three cathodic polarization curves 1, 2 and 3 (Fig. 11).

Fig. 11 contains a great deal of information with regard to the passivity behavior of anodic curves A and B. The cathode polarization line 1-1 intersects curve A at only one point (1A), indicating that metal A passivates spontaneously. However, it crosses curve B at three points (1B, 1B' and 1B''), showing that metal B may be either passive (1B) or active (1B'') depending on the potential of the system. The middle point (1B') is electrically unstable.

The effect shown by the cathodic polarization curve 2-2 for metals A and B is completely different than the effects shown by curve 1-1.
Curve 2-2 shows metal A in a passive state at point 2A, while it indicates active corrosion for metal B at point 2B. Curve 3-3 is different than either curve 1-1 or 2-2, in that it indicates a passive state for metal A at point 3A and an active corrosion at point 3A" depending on the potential, while it shows an active corrosion for curve B at point 3B. Points 1B' and 3A' in the transition region are electrically unstable and they may lead to pitting if the active regions are small compared to the passive area (120).

Fig. 11. Effect of Anodic and Cathodic Polarization on Passivity. A & B Anodic Polarization; 1-1, 2-2 & 3-3 Cathodic Polarization
Passivity largely depends on the type of metal, the environment, the chloride and oxygen content of a solution and temperature (121, 122).

Types and Forms of Corrosion

Corrosion is classified in several ways. It could be wet or dry, depending on the presence or absence of water or moisture. Corrosion is sometimes referred to as internal or external, depending on the surfaces of contact of the corroding structure with the corrosive medium. In other instances, corrosion is classified as physiochemical versus biological. The above are some general classifications of corrosion. In more specific cases, corrosion is classified into a more diverse form depending on the causes of corrosion and their mechanisms (4, 124, 125).

- Uniform or general Corrosion
- Pitting Corrosion
- Galvanic Corrosion
- Crevice Corrosion
- Stress Corrosion Cracking (SCC)
- Intergranular Corrosion
- Corrosion Fatigue
- Hydrogen Damage
- Erosion Corrosion
- Fretting Corrosion
- High Temperature Corrosion
- Stray Current Corrosion
- Dealloying or Selective Leaching
- Biological Corrosion
- Cavitation Corrosion
- Filiform Corrosion
- Knife Line Attack (KLA)
- Exfoliation

Uniform or General Corrosion

A general wearing away of a metal or an alloy in which the rate of corrosion is the same for the entire surface.
Pitting Corrosion

This is a form of a highly localized corrosion that results in the formation of pits or cavities in the metal surface, usually due to the rupture of protective films (124). Pitting is considered to be one of the most destructive forms of corrosion in transport pipelines, ships and liquid storage vessels.

Galvanic Corrosion

This is defined as the corrosion of two dissimilar metals in direct contact exposed to an electrically conductive medium. The less reactive metal acts as the cathode with very little corrosion or no corrosion at all while the corrosion of the other metal (anode) is substantially increased.

Crevice Corrosion

A form of localized corrosion caused by the differences in metal ion or oxygen concentration within crevices. The formation of concentration cells is encouraged in shielded areas due to stagnant solutions and surface deposits on the metal.

Stress Corrosion Cracking (SCC)

This form of corrosion is due to surface tensile stress in a corrosive environment. The tensile stress may be either residual or applied. The simultaneous action of both high tensile stress and corrodent on a metal cause cracks in the metal leading to premature and unexpected failure of the metal (4).

Intergranular Corrosion

This is a localized attack at the grain boundaries of an alloy leading to the disintegration of the grains and the failure of the
structure. It is generally caused by depletion or enrichment of an alloy element or by impurities at the grain boundaries.

**Corrosion Fatigue**

Premature failure of a metal due to the combined effect of cyclic stresses and a corrosive medium (126).

**Hydrogen Damage**

Mechanical damage to a metal caused by penetration or presence of hydrogen. Hydrogen blistering and hydrogen embrittlement are caused by the diffusion of atomic hydrogen (H) into the microvoids of a metal resulting in the formation of molecular hydrogen (H₂) (4, 124). At high temperatures, hydrogen disintegrates oxygen-containing metals such as copper (4), and it decarburizes (removes carbon) steel.

**Erosion Corrosion**

This is an increase in corrosion damage by the mechanical abrasion of protective films from a metal, generally due to a high velocity, turbulence or impingement effects in a corrosive medium (124, 126).

**Fretting Corrosion**

This is a special case of erosion corrosion that occurs in the atmosphere. Fretting corrosion is caused by the relative motion of two contacting surfaces, usually due to vibration, slip or frictional wear. This form of corrosion is common in automotive parts and other machinery where the protective surface films are destroyed leading to local concentration cells (4, 124).

**High Temperature Corrosion**

As its name implies, it is the corrosion of molten metals with gases and salts at elevated temperatures in the absence of an aqueous
phase (124).

**Stray Current Corrosion**

Localized electrolytic corrosion, usually caused by an external circuit, due to uncontrolled currents. The point at which the current leaves the metal acts as the anode, and therefore it corrodes (124).

**Dealloying or Selective Leaching**

The preferential removal of one or more electrochemically active metals from an alloy in a corrosive medium. Dezincification of brass and graphitization of cast iron are the examples of such corrosion. Leaching of Zn and Fe from brass and cast iron selectively, weakens the metals, leaving behind redeposited copper and weak graphite flakes in brass and cast iron respectively (124).

**Biological Corrosion**

Corrosion reactions that are mediated or enhanced by biological organisms such as bacteria, algae and fungi, usually through their metabolic by-products or deposits.

**Cavitation Corrosion**

This type of corrosion is caused by the repeated collapse of vapor bubbles or cavities on a metal surface in a high velocity liquid of changing pressure conditions. The collapse of the vapor bubbles destroys the protective films that leads to further corrosion damage.

**Filiform Corrosion**

This is a special kind of crevice corrosion, normally occurring under protective films in the form of thin, red-brown corrosion filaments (4).
Knife-line Attack (KLA)

This form of intergranular corrosion occurs in stabilized austenitic stainless steels due to welding, usually in the shape of thin lines adjacent to the weld (4). It is caused by solution and precipitation reactions of the alloying elements and compounds.

Exfoliation Corrosion

This form of corrosion is common in aluminum alloys, in which the metal corrodes in the form of layers or leaves (125).

The classification of corrosion into various forms is necessary for recognizing the causes and mechanisms of corrosion for their effective control. Many of these forms of corrosion may occur in a single structure at the same time.

Factors Affecting Corrosion

There are dozens of factors and environmental conditions that affect the corrosion of metals. These include parameters that are related to the metallurgy of the metal; factors related to the composition of the electrolyte as well as those related to the design and nature of the environment. These factors include:

- Electrode potentials
- Velocity of flow
- Dissolved oxygen
- Temperature
- Chlorine residual
- Static and cyclic loading
- Ionic strength
- Tensile stress
- Total dissolved solids
- Precipitation
- Hardness (Ca & Mg)
- Differential heating, welds
- Chloride
- Preexposure to chemicals, air
- Sulfate
- Differences in concentration/crevices
Some of the factors are interrelated, for example, electrode potential, dissolved oxygen, chlorine residual and total dissolved solids determine the oxidizing or reducing capacity of the solution. Alkalinity, hardness, ionic strength, total dissolved solids, carbon dioxide, pH and buffer capacity as well as chloride, sulfate and silicate determine the precipitation and complexation of these species in the electrolyte. Dissolved oxygen, CO₂, H₂S as well as ionic strength, total dissolved solids, color and organic matter influence the diffusion rates of the reacting species in the solution. The type of metal, its purity, temperature, heat treatment, surface roughness passivity and polarization along with anode, cathode areas in a specific solution determine the rate of corrosion of that metal.
Methods of Mitigation of Corrosion

Complete elimination of corrosion is impossible, since corrosion reactions are thermodynamically favored. There are several ways to minimize or inhibit corrosion:

1. Proper selection of the material
2. Adequate design of the system
3. Cathodic protection
4. Anodic protection
5. Use of inhibitors
6. Alteration of the environment
7. Use of coatings and paints.

Materials Selection

The choice of a suitable material for good corrosion resistance in a specific environment depends on many factors. Several alternative materials should be compared and evaluated on the basis of their cost, availability, maintenance, installation, weldability, fabrication, metallurgy, mechanical properties and their resistance to corrosion under similar conditions. The material that is the most economical should be selected.

Adequate Engineering Design

It is often said that corrosion starts at the drawing table where the actual design is initiated. A faulty design will cause severe corrosion, even in materials that may be highly resistant to corrosive attack. Many types of corrosion are affected by the design of a system including crevice corrosion, stress corrosion cracking, erosion
corrosion, galvanic corrosion fatigue and fretting (124, 127).

Corrosion could be drastically retarded by using sound design judgement in designing the various components of a system. Some of the important design considerations include avoiding dead ends and stagnant areas, use of welds instead of rivets, providing adequate drainage where it is needed, selecting appropriate flow velocity, selecting appropriate thickness of the metal, eliminating shielded areas, avoiding electrical contacts between dissimilar metals, reducing mechanical stresses, avoiding uneven heat distribution, eliminating harmful area effects, avoiding sharp turns and elbows, adequate insulation and choosing a proper shape and geometry of the systems. A good design should also include easy access to the structure, for periodic inspection, maintenance and replacement of damaged parts (127).

Cathodic Protection (CP)

Since corrosion is an electrochemical process in which the current flows between anode and cathode resulting in corrosion of the anode, it could be effectively stifled if either anode, cathode or both electrode reactions are eliminated. Cathodic protection is the supply of electrons or external current to the corroding metal to reverse the anodic reaction (Eq. 11), and thus force the metal to behave as a cathode.

\[
\text{Fe} = \text{Fe}^{++} + 2 \text{e} 
\]  

Cathodic protection could be easily described by polarization curves. Fig. 12 indicates that a freely corroding metal will enter solution as
positive ions at a current density $I_{\text{corr}}$. and at a corresponding potential of $E_{\text{corr}}$. The anodic reaction will not take place if $E_{\text{corr}}$ is less than or equal to the open circuit or reversible potential of the anode. The amount of impressed current required to shift the potential $E_{\text{corr}}$ in the cathodic direction so that $E_{\text{corr}} < E_a$, is called the protection current, $I_{\text{prot}}$. (4, 123, 128).

Cathodic protection is achieved by two ways: 1) impressed currents, and 2) sacrificial anodes.

![Schematic Presentation of Cathodic Protection](image)

Impressed current is usually applied by an external dc power supply to the metal to be protected with the use of an inert anode such as graphite. A sacrificial anode provides cathodic protection of a metal through appropriate galvanic coupling. Examples of sacrificial anodes are Zn, Mg, Al and their alloys (4, 128). The zinco coating of a
galvanized steel is also a form of cathodic protection by galvanic coupling. Zinc, the more reactive metal acts as the anode, therefore protecting steel. Cathodic protection has been in use for almost 160 years (4).

**Anodic Protection (AP)**

Anodic protection is reduction in the rate of corrosion of an active-passive metal by impressing an anodic current so that the potential is shifted in the anodic direction from the active to the passive state (4). Anodic protection, compared to cathodic protection is relatively new. It was developed less than three decades ago.

In order to anodically protect a metal, the potential must remain in the passive region. The control of potential is very crucial for effective AP, and a potentiostat is normally used for this purpose (Fig. 13).

From the curve in Fig. 13, it is evident that the anode corrodes at the rate of \( I_{\text{corr.}} \) in the active state. However, when anodic current, greater than \( I_{\text{corr.}} \) is impressed, the potential increases until it reaches the primary passive potential at the maximum critical current at point A. With further increase of the impressed current, the metal passivates. The corrosion rate is now decreased from \( I_{\text{corr.}} \) to \( I_{\text{pass.}} \). Anodic protection is applicable to all corrosive environments whether weak or strong. In contrast CP is only applicable to weak and moderately corrosive environments (4, 128).

**Use of Inhibitors**

These are a wide variety of organic and inorganic chemicals or chemical compounds, which, when added in small concentrations to a
solution, reduce the rate of corrosion. Inhibitors reduce corrosion by scavenging certain ingredients from the electrolyte, by physical adsorption, or by chemical action (4, 124). Inhibitors usually retard the rate of corrosion by forming thin protective films on metal surfaces. Such films are called cathodic inhibitors if they are formed by precipitation of corrosion reaction products at the cathodic sites.

![Diagram](image)

If they are formed by the passivation of the metal surface, they are called anodic inhibitors (129). Inhibitors decrease corrosion rates by increasing the polarization of the anode, cathode or both. They also lower the rate of corrosion by increasing the electrical resis-
tance in the circuit. Typical inhibitors include arsenic and antimony ions, sodium sulfide, hydrazine \((N_2H_4)\), chromates, nitrate, phosphate and silicate. Unfortunately, due to their toxicities, most of these inhibitors except the last two cannot be used in drinking waters (4).

**Alteration of Environment**

Corrosion can be reduced by changing certain environmental conditions that enhance the corrosion attack. These include removal of carbon dioxide, pH adjustment, reducing or adjusting the velocity of flow, lowering the temperature in hot water systems and the removal of oxygen or oxidizing agents (4).

**Coatings and Paint**

No discussion of corrosion control would be complete without mentioning the diverse group of coatings that are available for the protection of metals. Coatings are used primarily to physically isolate the metal from the corrosive medium. Zinc coating of steel is an exception, where Zn is employed as a sacrificial anode.

There are three types of coatings: 1) metallic coatings, 2) inorganic coatings and 3) organic coatings. Metallic coatings are applied by hot dipping, cladding, spraying and electroplating. Inorganic coatings include cement lining, glass coatings and porcelain enamels. Other types of inorganic coatings include conversion coatings which are formed by chemical conversion of the metal surface by reaction with the coating material. Chromatic and phosphate coatings are examples of this kind. Oxide coatings include those formed by the anodic oxidation of metal surfaces to form adherent oxide films, such as anodized aluminum, \(Al_2O_3\) and oxide of black steel, \(Fe_3O_4\) (130).
Organic coatings include a wide variety of paints, resins and varnishes.

**Measurements of Corrosion Rates**

Corrosion testing is a vital part of any corrosion control program. Corrosion rates can be determined by two methods: 1) the weight loss method, and 2) by electronic means.

**Weight Loss**

The conventional weight loss technique of measuring corrosion rates is a widely accepted test in many environments. The weight of the specimens or coupons is measured by means of an analytical balance before and after immersion in the test solutions. The loss in weight due to corrosion is converted into a uniform rate of corrosion, using the following expression (4):

\[
\text{mpy} = \frac{534 \ W \ (mg)}{D \ (g/cm^3) \cdot A \ (in^2) \cdot t \ (hr)}
\]

where

- mpy = corrosion rate in mils (0.001/in.) penetration per year
- w = weight loss
- D = density of the specimen
- A = area of the coupon
- t = exposure time

Corrosion rates can also be expressed in mm/yr., or mg/(dm^2)(day) or any other appropriate units.

Weight loss test results do not measure localized corrosion, but are an excellent method for measuring general or uniform corrosion.
Weight loss determinations are easy to make, and do not require sophisticated equipment.

**Corrosion Rates by Electronic Means**

Corrosion rates can be measured by electronic means employing electrochemical techniques or electrical resistance. The former is based on the electrochemical theory of corrosion using controlled potential or current to study the polarization of the electrodes. The latter depends entirely on the electrical resistance of the corroding surface.

**Electrochemical methods**

This constitutes a diverse group of corrosion rate measurements under various conditions. Although the electrochemical theory of corrosion was advanced by Whitney (131) in 1903, it was not until mid-1950's that electrochemical tests became an integral part of corrosion testing. In contrast to the weight loss method, electrochemical tests require sophisticated instrumentation including potentiostats, galvanostats, sweep generators, pulse generators, electrometers, null resistance ammeters, ammeters, oscilloscopes or recorders (132).

Electrochemical tests can be divided into two main groups, namely static or dynamic. The static tests are based on polarization of an electrode by a constant potential or current while recording the corresponding current or potential against time.

The dynamic tests polarize the specimen by a variable potential or current, while the variation in the observed current or potential
is recorded. Dynamic tests are further divided into three classes on the basis of the variation of polarization: 1) linear polarization sweep, 2) pulsed polarization or sinusoidal modulation, and 3) small perturbation around the corrosion potential (132).

The various types of electronic tests are included in Fig. 14. The linear polarization method and the electrical resistance method, measure the instantaneous rates of corrosion. The linear polarization method is based on the Stearn-Greary relation (133). The polarization method presumes that a small perturbation of potential, usually 5 to 20 millivolts over the corrosion potential, is linear. Corrosion rates can be calculated from the slope of the polarization curves when Tafel* slopes are known.

\[ I_{\text{corr.}} = \frac{\beta_a \beta_c}{2.3 (\beta_a + \beta_c)} \cdot \frac{\Delta I_{\text{app}}}{\Delta E} \quad \text{(Stearn-Greary Eq.) (56)} \]

where

- \( \beta_a \) = anodic Tafel slope
- \( \beta_c \) = cathodic Tafel slope
- \( \Delta I_{\text{app}} \) = the applied current
- \( \Delta E \) = the change in potential due to applied current

The various parameters used in equation 56 are presented in Fig. 15 for a typical electrochemical reaction (134).

* The slope of the anodic and cathodic polarization curves in the vicinity of corrosion potential \( E_{\text{corr.}} \) i.e. \( \Delta E/\Delta I_{\text{app}} \).
Fig. 14. Classification of Electronic Tests

Electronic Tests

Electrochemical Methods

Electrical Resistance
\[ I = \frac{1}{R} \]

Static Tests
Constant E or I

Polarization Resistance
\[ R_p = \frac{\Delta E}{\Delta I} \]

Dynamic Tests
Variable E or I

Potentiostatic
\[ E = K \]
\[ I = f(t) \]

Intentiostatic
\[ I = K \]
\[ E = f(t) \]

Apply a fixed \( \Delta E \),
\[ I = f(\Delta E) \]

Apply a fixed \( \Delta I \),
\[ E = f(\Delta I) \]

Linear Sweep

Pulsed Sweep

Potential Pulse
\[ \frac{\Delta E}{\Delta t}; I = f(t) \]

Current Pulse
\[ \frac{\Delta I}{\Delta t}; E = f(t) \]
Polarization resistance measurements are made using either a two electrode or a three electrode system. In the two electrode systems, both electrodes are identically made from the metal that is going to be tested. A three electrode system uses a third electrode as a reference electrode. In addition to the two identical electrodes, commercial probes with both two or three electrodes are available to measure the instantaneous rates of corrosion. The electrodes and the instrumentation are calibrated such that the rate of corrosion is measured directly in mils per year (135, 136).
Electrical resistance method (ERM)

This method of corrosion rate determination involves the change in electrical resistance of a corroding conductor (134). As the metal corrodes, its cross sectional area reduces, which causes a decrease in the current. By monitoring the change in the current, the rate of corrosion can be measured.

Limitations of Laboratory Testing

Although instantaneous corrosion rate determinations possess certain advantages over the weight loss methods, there are also some limitations. The advantages of instantaneous corrosion rates over weight loss techniques are their ability to collect data in a short time and their ability for in situ monitoring of the rate of corrosion. Polarization resistance can also be used to evaluate inhibitors for corrosion control.

The advantage of an electrical resistance method is that it does not require that the corroding medium be a liquid, since it does not depend on the electrolytic properties of the solutions. Its disadvantage is that the formation of conducting films and corrosion products on the corroding surface will give erroneous results (134).

Some of the limitations of the polarization resistance method are:

1. It is only a measure of the instantaneous rate of corrosion, and the corrosion rate may change with time.

2. The Stearn-Greary Equation is only valid when $\Delta E$ is equal to zero.
Non-linearity of the polarization curves in the vicinity of corrosion potential leads to errors.

3. The Stearn-Greary relation is valid if the process is under activation control. Diffusion overpotential causes errors in the readings.

4. The Tafel slope values, $\beta_a$ and $\beta_c$, may change during the experiment.

5. The presence of interfering redox reactions that do not take part directly in the corrosion reactions alter the true rate of corrosion.

6. The formation of films and corrosion products disturbs the surface and increases the resistance in the circuit, thereby causing some error.

Both weight loss and electronic methods of corrosion testing are helpful and complementary to each other. Both methods are affected by the shape and geometry of the electrodes or coupons, the surface area, rate of flow, the presence or absence of gases and the relative position of the electrodes in an electrolyte.

**Previous Investigations**

Corrosion of metals is not new. The corrosive action of water on lead pipes was noted by Galen in the second century of the Christian era, and the use of lead pipes for water supplies was forbidden during the time of Caesar Augustus (23). The earliest use of copper for water pipes by ancient Egyptians dates back to 2750 B.C. A copper pipe, three inches in diameter and 900 feet long was fabricated from sheet with a continuous joint (137). Wood pipes were used in the first
municipal water system built in U.S. at Boston in 1652 (138). The use of cement pipes over cast iron pipes for water supplies were favored by Crilly in 1908, because of the former's superior resistance to corrosion (139).

Although the galvanic nature of corrosion was advanced by Fabbroni in 1792, it was not until 1903 that Whitney suggested that the corrosion of iron in an aqueous solution was electrochemical (131, 140). Studies by Evans and Hoar (141), Brown and Mears (142) later confirmed the electrochemical theory of corrosion. The mixed potential theory of corrosion by Wagner and Traud (143), and the application of thermodynamics in studying polarization curves by Pourbaix (144) provided a further theoretical base for the electrochemical theory of corrosion. Details of corrosion processes can be found in classic corrosion literature by such authors as Evans (145), Uhlig (146), Pourbaix (116, 147), Fontana and Green (4), Ailor (148) and others.

**Corrosion of Iron and Mild Steel**

Rusty or red water, tuberculation of iron pipes, loss in carrying capacity of pipes and staining of fixtures are but some of the symptoms of corrosion in drinking water systems. A survey of corrosion literature indicates that research on the corrosion of potable waters did not start until the turn of the 20th century. The corrosivity of water and the factors causing corrosion have been studied by a number of investigators. Brown in 1904 (149) indicated that iron bacteria played an important role in corrosion of water pipes. The bacterial corrosion of iron and steel were also discussed by Beckwith (150), in which he demonstrated that corrosion of iron and steel was caused by the end
products of the metabolism of two types of sulfur bacteria. The anaerobic type that produces hydrogen sulfide by reduction of sulfate, and the aerobic type that produce sulfuric acid by oxidation. The association of bacteria with corrosion of iron in water mains was noted by Wolzogen Kuhr and Van der Vlugt (151). They showed that aerobic bacteria cause the formation of tubercules in water pipes, while anaerobic bacteria further enhance the rate of attack within the tubercules. An excellent review with some case histories of microbial corrosion in water was discussed by Kobrin (152). Kobrin classified corrosive microbes into four groups comprised of algae, bacteria, fungi and yeast.

Walker et al. in 1907 (153) suggested that the rate of corrosion of steel in an aqueous solution was a linear function of the oxygen content of the water. Friend and Brown in 1911 (154) studied the corrosion of iron in several salt solutions and determined that the rate of corrosion was influenced more by the anion than by the cation. Cox and Roetheli (155) investigated the rate of corrosion of steel in water containing varying amounts of dissolved oxygen. A linear relationship between the rate of corrosion and oxygen concentration was reported at dissolved oxygen concentrations up to 9 mg/l. The rate of corrosion was reported to decrease when oxygen concentrations were increased beyond 9 mg/l.

Tillmans and Heublein in 1912 (156) suggested the use of a calcium carbonate coating to prevent corrosion. Baylis in 1915 (157) studied the cause of tuberculation in iron pipes and used lime for treating the water to eliminate corrosion and red water complaints, at Jackson,
Mississippi. This was one of the early uses of lime for corrosion control. Lime treatment was also employed in Baltimore, Maryland for corrosion control by Baylis in 1919 (157), which later (158) led to the use of calcium carbonate precipitation for corrosion control. In 1936, Langelier (80) derived the calcium carbonate saturation index.

\[
\text{LSI} = \text{pH}_a - \text{pH}_s = \text{pH} - K + \log \text{Ca}^{++} + \log \text{Alk.} \tag{57}
\]

in which LSI is the Langelier Saturation Index; \(\text{pH}_a\), the actual pH of water and \(\text{pH}_s\) the pH at saturation with \(\text{CaCO}_3\). \(K\) is the \(\log \frac{K_S}{K_2}\); \(K_S\) the solubility product constant for \(\text{CaCO}_3\) and \(K_2\) is the ionization constant for the carbonate equilibrium, both corrected for ionic strength and temperature. \(\text{Ca}^{++}\) is in mole/1, while alkalinity is in equivalent/1 (159). Equation 57 is the simple form of the Langelier index that is applicable in the pH range 6.5 - 9.5. The Langelier index is an indicator of the tendency of a water to dissolve or precipitate calcium carbonate. A positive value of LSI indicates supersaturation with \(\text{CaCO}_3\), a tendency to precipitate \(\text{CaCO}_3\). A negative value is indicative of undersaturation, a tendency to dissolve \(\text{CaCO}_3\).

In 1944, Ryznar (97) developed an empirical formula using the Langelier's \(\text{pH}_s\) to predict the corrosivity of a given water.

\[
\text{RI} = 2\text{pH}_s - \text{pH}_a \tag{58}
\]

in which RI is the Ryznar Index, \(\text{pH}_s\) is the pH at saturation with \(\text{CaCO}_3\); and \(\text{pH}_a\) is the actual pH of water. An RI value above 7 indicates corrosion and below 6.5 shows encrustation.
In 1948, Loschiavo (160) proposed the Calsil Index, CI for the prediction of corrosion in soft waters.

$$CI = \frac{Ca + Mg + HSiO_3 - Anions}{2}$$  \hspace{1cm} (59)

where all concentrations are expressed in milliequivalent/l. A negative value of CI means very corrosive, greater than 0.1 non-corrosive, and between 0 to 0.1 slightly corrosive.

Dye (99) in 1958 proposed the momentary excess, ME to predict the CaCO₃ precipitation.

$$ME = \frac{Ca^{++} + CO_3^-}{2} - \left[\frac{(Ca^{++} + CO_3^-)^2}{2} - (Ca^{++} \times CO_3^-) + K_s \times 10^{10}\right]^{1/2}$$  \hspace{1cm} (60)

where Ca^{++} and CO_3^- are both expressed as mg/l CaCO₃. In 1960, McCauley (98) introduced the driving force index, DFI, using the solubility expression for CaCO₃.

$$DFI = \frac{(Ca^{++}) \times (CO_3^-)}{K_s \times 10^{10}}$$  \hspace{1cm} (61)

where the concentrations are in ppm, as CaCO₃.

The Aggressive Index, AI (1), approved by AWWA Board of Directors on January 30, 1977 for asbestos-cement pipe is defined as:

$$AI = pH + \log (AH)$$  \hspace{1cm} (62)

where A is the alkalinity and H is the calcium hardness of the water, both expressed as mg/l CaCO₃. A value of AI less than 10 is interpreted as very aggressive; above 12 non-aggressive, and between 10 to 12 moderately aggressive.

Riddick (100) developed an empirical index, the Riddick Corrosion Index, RCI in which he included several factors that affect corrosion
such as dissolved oxygen, chloride ion, noncarbonate hardness, nitrate and silica.

\[
\text{RCI} = \frac{75}{\text{Alk}} \left[ \text{CO}_2 + \frac{1}{2} (\text{Hardness} - \text{Alk}) + \text{Cl}^- + 2\text{N} \right] \frac{10}{(\text{SiO}_2)} x \frac{\text{DO} + 2}{\text{Sat DO}}
\]  

(63)

where all parameters are expressed in mg/l except alkalinity and hardness which are both expressed as mg/l CaCO₃. The values of RCI are interpreted as:

0-5 extremely non-corrosive

0-25 non-corrosive

26-50 moderately corrosive

51-75 corrosive

76-100 very corrosive

101+ extremely corrosive

Lucey (161) proposed a pitting propensity index for copper pipe based on chemical quality of the water including pH, DO, Cl⁻, SO₄²⁻, Na⁺ and NO₃⁻ ions. A nomograph was developed to evaluate the pitting tendency of copper as detailed by Pathak (162).

Roetheli and Brown (163) studied the rates of corrosion of steel as affected by rotational velocity of flow in oxygenated waters. The rate of corrosion was reported to increase as the rotational velocity of water increased to about 120 revolutions per minute, RPM. The rate of corrosion declined with further increase of the speed of rotation until it reached a minimum value at 260 RPM. At speeds above 260 RPM, the rate of corrosion increased again primarily due to erosion.
Larson explained (164, 165) that both flow velocity and oxygen can accelerate corrosion or inhibit corrosion depending on the mineral quality of the water.

Volkening (166) studied the effect of chlorine dosage (0 to 4.0 ppm) and velocity (0.1 to 6.4 fps) on the rate of corrosion of mild steel pipes in seawater. The rate of corrosion by weight loss and pitting measurements were compared. Pitting measurements were made using a pointed micrometer and the average of the ten deepest pits was reported as the average pit depth for each pipe specimen. The rate of corrosion by weight loss increased with increasing velocity and increasing chlorine residual. Pitting rates were greater than average corrosion rates determined by weight loss. The effects of pH and velocity on corrosion of steel water pipes were investigated by Eliassen and co-workers (167) in both short and long-term studies. The rate of corrosion was shown to increase with increasing velocity of flow. The change in pH in the range 5.5 - 9.0 had little effect on the rate of corrosion. However, serious pitting was reported to occur at pH 6.5.

The effects of mechanics of flow on corrosion of metallic pipes were investigated by Romeo and associates (168) under both laminar and turbulent flow conditions. These investigators concluded that Reynolds number, velocity, pipe size and length and the surface condition of the pipe are all important. The rate of corrosion determined under different hydraulic conditions cannot be compared on the basis of the velocity of flow. For example, it was cited "That at the same velocity, the rate of corrosion was inversely proportional to the internal diameter of the pipe raised to the 0.125 power" (168:20).
Copson (169) discussed the effect of velocity of fluids on the rate of corrosion of iron and several other metals. He assessed that the velocity effects should be studied under different conditions for different metals. It was shown that velocity had varied effects on the rate of corrosion depending on pH, oxygen, galvanic couplings, polarization and electrode potentials.

An excellent review of the effects of velocity and other water quality parameters on the rate of corrosion of galvanized steel and galvanized wrought iron pipe in several domestic waters was prepared by the NACE* Technical Committee T-7 on potable waters (170). Studies by Dahljelm (171) and Clark (172) showed that corrosion in distribution systems could be controlled by chemical treatment of water, particularly pH adjustment, using sodium hydroxide and soda ash.

Hatch and Rice (173) studied the influence of water composition on the corrosion of steel under laboratory conditions. Using calcium salts of Cl\(^-\), SO\(_4\)\(^-\) and HCO\(_3\)\(^-\) and distilled water in his experiments, he found out that the rate of corrosion was higher in SO\(_4\)\(^-\) solution compared to Cl\(^-\) solution, at anion concentrations of 0 to 100 ppm. The rate of corrosion of steel in HCO\(_3\)\(^-\) solution was reported to be extremely low. They also studied the inhibitory effect of HCO\(_3\)\(^-\) on the corrosion of steel in chloride and sulfate solutions.

Larson and Solo (72) investigated the loss in water main carrying capacity, and noted that it is caused by tuberculation, sludge deposits (delayed precipitation) and microbial growths. Deposits of magnesium

*National Association of Corrosion Engineers
hydroxide and aluminum hydroxide, due to their incomplete precipitation in the treatment plant and thus to post-precipitation in the system, restrict the flow of water. Gosh (174) studied the deterioration of waters in distribution systems in five communities in Maine. The waters were soft, all having negative saturation indices and low buffer capacities. The use of lime and soda ash for control of corrosion was recommended.

The effect of pH on the quality of CaCO₃ scale deposited in moderately hard and hard waters, using a cast iron rotating-disc electrode was investigated by McClanahan and Mancy (175). They found that soft water inhibition proved difficult because of the porous nature of the CaCO₃ film and its low rate of deposition. The effect of pH on the permeability of the deposited scale was insignificant.

Larson and Skold (126) examined the effect of pH, velocity, Cl⁻, SO₄²⁻, HCO₃⁻, chlorine and calcium on the rate of corrosion of steel and cast iron in air saturated systems under laboratory conditions. They reported that the rate of corrosion was dependent on the ratio of Cl⁻ and SO₄²⁻ ions to HCO₃⁻, CO₃⁻ and calcium ions. Velocity was shown to exert both corrosive and inhibitive effect depending on the concentrations of the anions in the solution.

The significance of corrosion control in domestic waters was summarized by Lane (176). Both surface and ground waters should be properly treated such that the saturation index is positive, have adequate calcium and alkalinity, with low Cl⁻/HCO₃⁻ ratio. Yapijakis (177) outlined the control of corrosion in distribution systems.
Selection of proper materials, use of protective coatings, adequate insulation, degassification (removal of $O_2$, $CO_2$ and $H_2S$), chemical treatment of water (pH adjustment and use of inhibitors) and cathodic protection were considered necessary to combat corrosion.

Corrosion rates of mild steel and cast iron specimens were investigated by Skold and Larson (178) in 1957. Both weight loss and instantaneous polarization techniques were used for corrosion rate measurements. They found out that a logarithmic relationship existed between the rate of corrosion by the weight loss method and the polarization resistance, $\Delta E/\Delta I$, at low current densities.

Stumm (179) determined the rate of corrosion of cast iron specimens in water using the polarization resistance technique. He observed that the corrosion current was a linear function of the reciprocal polarization resistance, $\frac{\Delta I}{\Delta E}$ when I approached zero. He further noted that the deposition of protective CaCO$_3$ coating decreased the rate of corrosion by "ennoblement" (179:1489) of the corrosion potential. In a separate paper, Stumm (180) evaluated the effects of pH, buffer capacity, CaCO$_3$ deposition, oxygen and alkalinity on the rate of corrosion of cast iron using the weight loss method. He concluded that the rate of corrosion was higher in waters of low buffer capacity. He suggested that buffer capacity of water inhibits corrosion by improving the passivity behavior of dissolved oxygen. It was also noted that in aerated waters, the rate of corrosion was primarily under cathodic control, particularly for the initial exposure of the specimens.

In evaluating protective calcite coatings on pipe surfaces, McCauley (181) noted that hydraulic considerations such as turbulence
and velocity of flow, and the surface conditions of the pipes are important. Increasing velocity of flow decreases the thickness of the laminar film adjacent to the pipe wall and facilitates the rate of diffusion of calcium and carbonate ions to the surface. The rate of transfer of oxygen from solution to the metal surface is similarly affected by increased flow velocity.

A two year study on the corrosion of copper, galvanized steel, black iron and aluminum, in thirty different American and Canadian potable water supplies was conducted by the National Association of Corrosion Engineers (182). The experiments were performed in hot or cold water service lines. No weight loss or pitting measurements were made in their study. The samples were only visually evaluated at the end of the exposure time. The sources of water, their analytical quality and the type of treatment they received were reported. Both Langelier and Ryznar indices were calculated using the chemical analysis of the test waters. From the visual observations it was concluded that black iron showed both pitting and tuberculation. The appearance of aluminum specimens was different depending on the pH of the solution. Aluminum corrosion was shown in low pH, copper bearing waters. No correlation between Langelier index and aluminum corrosion was observed. Galvanized steel was shown to corrode in some waters, particularly those containing copper ions. No rust spots on galvanized steel specimens were shown in several waters with negative Langelier index, while pitting was observed in one hot water system even with a high positive saturation index. The performance of copper was reported to be satisfactory.
Uhlig (183) described the effect of metal composition and structure on corrosion in aqueous media and at elevated temperatures. He suggested that in aqueous media, factors such as heat treat and cold work are important only if corrosion is controlled by diffusion. Metallurgical factors are not important. However, metallurgical factors play a role in localized corrosion.

The anticorrosion treatment of both surface and ground water supplies was reviewed by Dye (184). He recommended a saturation index* of 1.0 or more, a DFI* of 15-20 and an ME* of 12-15 for softened surface waters, with low calcium and high carbonate ion concentrations. Aerated lime-softened ground waters could be rendered unaggressive with a similar ME to that of surface supplies, but a lower DFI value. If such treatment caused excessive CaCO$_3$ deposition, a polyphosphate treatment of 0.5 ppm was recommended. The mechanism of the corrosion reactions, the application of electrochemical methods such as polarization resistance for determination of corrosion rates, the effect of inhibitors and the dual role of oxygen in retarding or enhancing the rate of corrosion were summarized by Schneider and Stumm (185).

Miller (186) detailed the effectiveness of cement-mortar linings in cast iron pipes. He indicated that such linings in thickness of 1/16 - 1/4 inch were effective in control of tuberculation and provided a Hazen-Williams flow coefficient (C) comparable to those of new pipes. Based on forty years of field experience, he emphasized that the success of cement lining in control of corrosion depends on the quality of

*Saturation Index refers to Langelier's Saturation Index
DFI is driving force index
ME is momentary excess.
lining in meeting the standard specifications. A number of factors related to corrosion of metals were reviewed by Larson (187). The role of oxygen, flow rate, pH, the use of CaCO$_3$ and the influence of ions such as Cl$^-$, SO$_4^{2-}$, Na$^+$, Ca$^{++}$, Mg$^{++}$ and silica were discussed. Chloride and sulfate were noted to enhance corrosion attack, while CaCO$_3$ and silica had the opposite effect.

Morris (188) and Fitzgerald (189) reviewed the causes of water main breaks. Among other factors, both internal and external corrosion were noted. The selection of proper piping materials for chemically treated potable waters was discussed by Lane and Neff (190). General guidelines and design considerations were discussed along with chemical treatment of water with lime, caustic soda, soda ash, sodium silicate, sodium polyphosphate and sodium zinc polyphosphate. The deterioration of water quality in distribution systems was studied by McClelland and Mancy (191), using a prototype water quality monitoring system. Among other parameters, CaCO$_3$ deposition tests for formation of scale and corrosion rate monitoring were reported. The rate of corrosion was measured with a 3-electrode Petrolite instrument* using the polarization technique. A current is impressed between working and counter electrodes to polarize the working electrode by 10 mv. The instrument is calibrated such that the current required for polarization is directly read in mils per year of corrosion rate.

Myers and Obrecht (192) summarized the factors and types of corrosion in potable waters. They indicated that both calcium and silica

* A product of Petrolite Instruments, 4411 Bluebonnet, Stafford Texas 77477.
retarded corrosion by the formation of protective coatings on ferrous materials, while \( \text{Cl}^- \), \( \text{SO}_4^{2-} \), \( \text{O}_2 \), \( \text{CO}_2 \), \( \text{H}_2\text{S} \), iron, ammonia, sulfide and nitrate were reported to accelerate corrosion in drinking waters. The susceptibility of ferrous and galvanized ferrous materials as well as copper to pitting corrosion were included in their report. With regard to the corrosion of copper, it was indicated that pitting is commonly observed in well waters containing high \( \text{CO}_2 \), \( \text{SO}_4^{2-} \), \( \text{Cl}^- \) and \( \text{HCO}_3^- \) ions and low hardness. A case history of failure of type 304 stainless steel microstainer screens in a water treatment plant, after 8 years of operation, was reported by Randolph and Lincoln (193). The cause of failure was identified as occluded cells or crevice corrosion.

The influence of nonchemical factors on the corrosion of metals in domestic waters was described by Sussman (194). The role of designers, architects, plumbers, maintenance personnel, government regulations as well as the effect of equipment, alteration or repair of materials in control of corrosion in potable water systems were mentioned. A short-term study of several plumbing materials was conducted by Ready (195) in Southern California waters. The metals studied included carbon steel, stainless steels types 304, 316 and 410, cupronickels, zinc, silicon bronze, red brass and copper. The rates of corrosion were determined by an electrical resistance technique using a Magna Corporation Corrosometer*. The test waters were very hard and alkaline. The rates of corrosion of copper, low zinc brass and bronze were found to be in the range 2.5 to 3 mpy, while those of cupronickels ranged from 0.5 to 1.5

* A product of Magna Instruments, a Division of Rohrback Corporation, 1186 East Telegraph Road, Santa Fe Springs, California 90670
mils per year. The rate of corrosion of zinc and carbon steels was the highest of all tested metals ranging from 9 to 21 mils per year. No corrosion was reported in all stainless steel tests.

McClanahan and Mancy (196) studied the effect of repeated polarization on the corrosion rate of cast iron samples, and compared the results with freely corroding samples. The results of the two methods of corrosion testing were reported to be in close agreement with one another. A long-term study of corrosion of several metals and alloys over a period of 7 - 15 years was conducted by Geld and McCaul (197). The test water was low in mineral content with total dissolved solids of 40 - 54 ppm and pH of 6.5 - 7.5. The tests were run in capped jars under stagnant conditions at room temperature. The test solutions were changed every six weeks. Corrosion was evaluated by measuring maximum pit depths at the end of the exposure times. General corrosion was reported to be low in comparison to pitting corrosion in aluminum, bronze, manganese bronze, type 416 stainless steel and galvanized iron samples. The maximum pit depth in copper and cupronickels was shown to be less than one mil for the entire duration of the tests. The mechanism of corrosion of iron in aqueous solutions was reviewed by Ammar (198). He proposed new reaction pathways for the anodic dissolution of iron in both acid and alkaline solutions. The formation of intermediate species such as (Fe(OH)₂, FeOH⁺ and Fe₂OH⁺ were discussed.

Bennett and co-workers in 1977 (199) reported an unusual form of corrosion in a water system of a Canadian town. They suggested that high-frequency alternating currents among other factors were responsible for excessive corrosion problems in the system. They suggested
that this type of corrosion be classified as "alternating current electrical corrosion" (199:30). The town is located in a discontinuous permafrost region with an average annual temperature of 27° F (-2.8° C).

**Corrosion of Copper and Zinc**

The use of brass and copper tubing for plumbing materials was discussed by Cole (200). Copper tubing was recommended for both hot and cold water lines, in waters of moderate carbonate hardness (60-120 ppm), having a pH value of 6.7 or higher. Brass pipes were preferred in waters with carbonate hardness below 60 or above 120 ppm. The treatment of both soft and hard waters was recommended for satisfactory use of copper plumbing using lime or soda ash. Asselin and Rohrman (201) studied the corrosion of copper in aerated sodium halide solutions at various temperatures. For the salts NaCl, NaBr and NaI, the rate of corrosion of copper was found to be the highest in NaI solution. The lowest rate of corrosion of copper was observed in NaCl solution. An analysis of results of a national survey of copper corrosion in domestic waters was reported by a corrosion task group (202). The alkalinity and pH of the water were shown to have significant effect on copper corrosion. The lower the pH, the higher the rate of copper corrosion. Other factors that affect copper corrosion included CO₂, dissolved oxygen, ammonia, manganese, chlorine and velocity of flow. The failure of copper tubing in hard waters because of carbon films that result from the annealing of the tubing was also discussed. The carbon films act as the cathode, thereby promoting anodic sites which
ultimately leads to pitting of the copper. The Langelier (80), Ryznar (97) and Riddick (100) indices were calculated and attempts were made to correlate them with the corrosion of copper tubing. No significant correlation was observed.

Obrecht and Quill, in a series of articles (203 - 209) discussed the results of laboratory and pilot plant testing of copper corrosion in domestic waters. The effects of temperature, alkalinity, oxygen, dissolved salts and pH as well as the type of treatment the water received on the rates of corrosion of copper and its alloys were investigated. It was found out that both deaeration and blending of zeolite-softened water with raw water reduced the pitting tendency, while high velocity and temperature accelerated the rate of attack of both copper and red brass. The lowest rate of corrosion of copper tubes was reported in the hard water tests, while the maximum rate of corrosion of copper was shown to occur at a temperature of 170°F (206).

Among the copper alloys, both cupronickel (90/10) and admiralty (71% Cu, 28% Zn, 1% Sn) tubing were shown to have excellent corrosion resistance in sodium zeolite softened water containing both oxygen and carbon dioxide (208). Obrecht and Quill (209) identified the velocity of flow, the service temperature, dissolved oxygen, carbon dioxide and hardness as important factors in corrosion of copper and red brass. Tracy (210) described the general ways in which copper and copper alloys corrode. The presence of oxygen or another oxidizing agent was considered a prerequisite for copper corrosion. Various forms of corrosion were briefly discussed. A case history of failure of copper tubing by pitting in a newly constructed residential area was presented
by Rambow and Holmgren Jr. (211). The ground water that caused severe pitting of copper plumbing was very high in total dissolved solids (1500 ppm), with a hardness of 735 mg/l; calcium, 225 mg/l; magnesium, 40 mg/l; chloride 160 mg/l; sulfate, 525 mg/l; bicarbonate, 360 mg/l; pH 7.1 and a free carbon dioxide content of 36 mg/l.

Levelton and Kilburn (212) studied the effects of water composition, velocity, temperature and surface condition of the pipe, on the rates of corrosion of seamless and seam-welded copper tubing in domestic waters, under laboratory conditions. Tests were also performed in domestic and industrial wastes. The tests on potable waters were conducted in circulating loops for exposure periods of 1 to 25 months at 180°F, using flow velocities of 2.5 and 12.0 fps. In the low flow velocity tests, carbon dioxide was also bubbled through the samples. Sewage tests were run in actual sewage streams from 104 to 160 days of exposure. Corrosion rates were determined by the weight loss method. It was concluded that hard, cold-worked copper specimens corroded more rapidly than soft specimens, and that the rate of corrosion was higher in the test containing carbon dioxide, despite its low velocity. The rate of attack at the fusion line of the seam-welded pipes was severe in industrial sewage, while no localized effect was observed in the potable water tests.

A new theory of pitting of copper water pipes and tanks was proposed by Lucey (213). He demonstrated that pitting of copper occurs by formation of cuprous chloride "pockets" (213:175) under a porous cupric oxide membrane when the $E_H$ of the solution is over 90 mv.

Mattsson and Fredriksson (214) investigated the mechanisms and causes
of pitting of hard-drawn copper tubing in potable waters under both laboratory and field conditions at temperatures of 40 to 80°C. Pitting was reported to be prevalent in waters of low alkalinity and low pH. The rate of attack of copper was correlated with the concentration ratios (mg/l) of $\text{HCO}_3^- / \text{SO}_4^-$ . It was suggested that low $\text{HCO}_3^- / \text{SO}_4^-$ ratio led to the formation and precipitation of basic copper sulfate scale that resulted in higher corrosion rates. At values of $\text{HCO}_3^- / \text{SO}_4^-$ >1, the precipitation of basic copper carbonate in the vicinity of the anodic site retarded corrosion. Cohen and Lyman (215) reported 71 cases of copper tubing failures in U.S. water supplies and sewage during a 5 year period. The types and/or causes of failure were classified as shown in Table 6. It was shown that all types of copper tubings (types K, L and M) were susceptible to corrosion. Waters that caused pitting were analyzed and found to have a broad range of chemical qualities. The pH values of the waters that supported pitting were between 6.4 and 8.2; chloride, (0-175 mg/l); sulfate, (0-700 mg/l) and dissolved carbon dioxide was 0-90 mg/l.

Myers and Obrecht (216) evaluated the use of copper and its alloys in domestic hot water systems. It was suggested that copper pipes should not be employed in aggressive waters, if flow velocities are higher than 4 fps and the water temperature is above 140°F. The use of 90-10 cupronickels were recommended for temperatures over 140°F and high water velocities.

The pitting of copper in southern California waters was studied by Cruse and Pomeroy (217). Rapid pitting of copper pipes in several
California waters was shown to have occurred in pipes of abnormal interior surface. Cornwell and Co-workers (218) investigated the effects of water quality, metal composition and carbon residues, on the occurrence of pitting of copper tubing under both laboratory and field conditions. It was concluded that pitting of copper was supported by deep well waters that are usually low in organic matter. The carbon residue on the bore of the tubing was also shown to have a significant effect on initiation of pitting attacks, while the metal hardness was shown to play no major role in pitting reactions. Composition of the copper was important. For example, addition of one percent tin to copper was reported to reduce pitting drastically. Pitting was evaluated by measuring the electrode potentials of the solutions. In copper pipes that contained carbon residues, the $E_H$ value increased until it reached a critical level, above which pitting occurred. In thoroughly cleaned pipes, containing no carbon residue, $E_H$ values did not rise and no pitting was observed in such systems.

Mattsson (219) reviewed the pitting of copper in hot and cold potable water systems. In cold water systems, the chloride ion was

<table>
<thead>
<tr>
<th>Type or Cause of Failure</th>
<th>Number of Failures</th>
<th>Per Cent Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pitting attack</td>
<td>24</td>
<td>33.8</td>
</tr>
<tr>
<td>Impingement</td>
<td>12</td>
<td>16.9</td>
</tr>
<tr>
<td>General Corrosion</td>
<td>3</td>
<td>4.2</td>
</tr>
<tr>
<td>Channel Attack (sewage drains)</td>
<td>8</td>
<td>11.3</td>
</tr>
<tr>
<td>Sulfide gas attack (sewage drains)</td>
<td>6</td>
<td>8.5</td>
</tr>
<tr>
<td>Underground corrosion</td>
<td>2</td>
<td>2.8</td>
</tr>
<tr>
<td>Faulty workmanship</td>
<td>8</td>
<td>11.3</td>
</tr>
<tr>
<td>Special cases</td>
<td>8</td>
<td>11.3</td>
</tr>
</tbody>
</table>
noted to cause pitting. In hot water systems, high sulfate content and the presence of manganese were reported to be responsible for pitting of copper. Several cases of copper tubing failure in both hot and cold water installed in the city of Rockville, Connecticut were reviewed by Newell (220). The city water was furnished from a lake with an extremely low total mineral content, and was treated for color removal, using alum, lime, and chlorine and had fluoride added. The treated water alkalinity was 10 mg/l and its pH about 7.6. The final chloride content of the water was 10 mg/l. Most of the failures were reported to have occurred in the hot water systems.

Zinc coating is applied to steel and iron in order to protect the base metals from corrosion. The protection of a zinc coating is achieved either through physical isolation of the base metal from the aqueous solution or by the electrochemical galvanic coupling of the zinc-iron system. The dezincification and Stress Corrosion Cracking of brass; and pitting and erosion corrosion of copper tubes in domestic waters were reviewed by Mattsson (221). The effects of pH, mineral content, temperature and surface conditions of the metal on corrosion were discussed. Bartow and Weigle (222) evaluated the presence of zinc in natural and potable waters. Several drinking waters in contact with galvanized iron pipes were reported to contain from 5 to 23 mg/l of zinc. Zinc concentrations of up to 50 mg/l were found in some natural waters. The corrosion rates of pure zinc (99.99% Zn) and galvanized steel were investigated by Kenworthy and Smith (223), at temperatures of 18°C and 85°C, in waters containing 0 to 79 mg/l of carbon dioxide. They found out that an increase in free CO₂ content
increased the rate of attack of both zinc and galvanized steel at both test temperatures. They further noted that pitting attack of zinc was more severe than of galvanized specimens.

Several researchers (224 - 227) have noted the failure of galvanized coatings in offering protection to steel, particularly at elevated temperatures. The effects of water composition and temperature on the reversal of the electrochemical behavior of high-purity zinc and commercial grade mild steel in aqueous solutions were extensively studied by Hoxeng and Prutton (226) in a series of short-term (6-96 hours) experiments. These authors concluded that in most cases zinc was found to be anodic to steel. However, changes in water quality parameters were found to cause a reversal of potential in the electrochemical behavior of zinc-steel couple, thus making zinc cathodic to steel. Zinc was found to be anodic to steel in the absence of dissolved oxygen. In the presence of oxygen, water quality parameters such as $Ca^{++}$, $Cl^-$, $SO_4^{2-}$ and silicate tended to give more anodic zinc potentials, while $HCO_3^-$ and $NO_3^-$ promoted the reversal of zinc potentials to more cathodic values. The role of temperature in the reversal of zinc potentials was considered less important than the role played by chemical composition of the test solutions.

Shuldener and Lehrman (228) in a study of the zinc-iron system showed that bicarbonate had a significant effect on the reversal of zinc potential as evidenced by rusting of the iron. In a separate short-term study, Shuldener and Lehrman (229), conducted experiments to determine the effects of varying ratios of iron to zinc areas on the rate of reversal of potential. They demonstrated that an increase
in the ratio of the iron to zinc area increased the rate of potential reversal in solutions of same chemical composition. Rice (230) reviewed the effects of water quality on the reversal of potential of zinc on galvanized steels and noted some of the disagreements and anomalies in the existing data. He also provided guidelines for successful use of galvanized pipes in domestic waters, such as maintaining water temperature below 140° F and avoiding coupling with copper as well as avoiding high water velocities.

Gouda and co-workers (231) studied the effect of several anions including $\text{SO}_4^{2-}$, $\text{Cl}^-$, $\text{Br}^-$, $\text{ClO}_4^-$, $\text{NO}_3^-$, $\text{NO}_2^-$, $\text{WO}_4^{-2}$, $\text{H}_2\text{PO}_4^-$, $\text{HPO}_4^{-2}$, and $\text{CrO}_4^{-2}$ on the corrosion of zinc in neutral, aerated solutions and in acid solutions. The steady state potentials of pure zinc electrodes in neutral solutions were measured and found to follow a logarithmic relation (Eq. 64) with respect to the concentrations ($C$) of the first six anions (231).

$$E = a - \log C$$  \hspace{1cm} (64)

where $a$ and $b$ are constants. As can be seen from the equation, an increase in concentration of $\text{SO}_4^{2-}$, $\text{Cl}^-$, $\text{Br}^-$, $\text{I}^-$, $\text{ClO}_4^-$ and $\text{NO}_3^-$ ions causes a decrease in electrode potentials of zinc. The following descending order, $\text{SO}_4^{2-} > \text{Cl}^- > \text{Br}^- > \text{ClO}_4^- > \text{NO}_3^- > \text{I}^-$ was observed in corrosion of zinc as promoted by the anions. The remaining anions, such as $\text{HPO}_4^{-2}$, $\text{H}_2\text{PO}_4^-$, $\text{WO}_4^{-2}$, $\text{NO}_2^-$ and $\text{CrO}_4^{-2}$ were shown to cause an ennoblement of the zinc potential, thus aiding in passivation of zinc and inhibition of its corrosion.

The passivation and pitting characteristics of high purity zinc in boric acid - sodium hydroxide buffer solutions were investigated by
Davies and Lotlikar (232). They concluded that in the absence of aggressive ions such as Cl\(^-\), the passivation of zinc was observed in the buffer solution in the pH range 9.2-12.3. At pH values out of this range, zinc corroded by general attack. The presence of Cl\(^-\) ion beyond a critical concentration was shown to initiate pitting attack by the breakdown of a zinc oxide and/or zinc hydroxide passive film. The pitting potentials of zinc solutions were found to be a function of applied current density, pH and chloride ion concentration.

Fraunhofer and Lubinski (233) conducted research on polarity reversal of a zinc-mild steel couple in London tap water and in several other aqueous solutions. The polarity reversal of the zinc-iron couple was shown to be aided by the presence of dissolved oxygen, bicarbonate, and nitrate ions in solution, while chloride and sulfate ions were shown to prevent such a reversal. It was further noted that polarity reversal of the zinc-mild steel couple occurred at a NaHCO\(_3\)/NaCl concentration ratio (ppm) of 20:1, indicating that polarity reversal in galvanized hot water systems is insignificant because of the low alkalinity of most potable waters. The effects of temperature (30\(^\circ\) C - 90\(^\circ\) C) on the behavior of the zinc-mild steel couple in a sodium borate-hydrochloric acid buffer solution of pH 7.60 were investigated by Ashworth and Fairhurst (234). No potential reversal was seen except, at a temperature of 90\(^\circ\) C, in an aerated solution containing chloride ions. Pitting of zinc was reported under all conditions of the tests, except in a deaerated solution at a temperature of 30\(^\circ\) C where zinc remained passive.
Abd El Haleem (235) studied the dissolution and pitting potential of zinc in $10^{-2}$ and $10^{-3}$ M KOH solution with and without the presence of Cl$^-$, Br$^-$ and I$^-$ ions. The rate of corrosion of zinc in the dilute (10$^{-3}$ M) KOH solution was enhanced by the addition of small amounts of aggressive Cl$^-$, Br$^-$ and I$^-$ ions, while the addition of $2 \times 10^{-4}$ M of the anions to the $10^{-2}$ M KOH solution did not alter the rate of corrosion of zinc, and passivation prevailed. At higher anion concentrations, a logarithmic decrease of the pitting potential of zinc was observed, implying pitting of zinc by aggressive anions through breaking of the oxide film. Muralidharan and Rajagopalan (236) evaluated the mechanism of passivation of zinc in dilute sodium hydroxide solution ($10^{-2}$ M) and concluded that passivation of zinc occurred due to formation of three monolayers on the active sites of the zinc surface. The discharge of hydroxyl ions was shown to be the rate determining factors in the passivation of zinc under their test conditions.

Scope of Study

From a thorough and critical review and analysis of existing corrosion literature, it is evident that most research in the field of corrosion is directed towards either the development of new corrosion resistant materials, or towards the study of corrosion in the chemical process industries. Drinking waters are dilute, heterogeneous solutions of electrolytes, to which the results obtained for the chemical process industries are seldom applicable. Furthermore, the choice of the materials of construction in potable waters is limited to only a few metals such as mild steel, ductile iron, galvanized steel and copper primarily due to physical and economic considerations. While much
research has been conducted on the corrosion of metals in specific
drinking waters, a comprehensive study evaluating the effects of
various water quality parameters on the rate of corrosion of these
metals in non-existant.

The research data in drinking waters is often incomplete and the
results are inconclusive. For example, many investigators have based
their conclusions on single tests and failed to run duplicate or
repeated tests. Still in other cases, the chemical composition of the
test waters were not given. The duration of tests, the volume of the
solutions and other experimental conditions are generally ignored in
many research publications.

The scope of this research was to investigate the influence of
various water quality parameters on the rates of corrosion of mild
steel, galvanized steel, and copper under controlled laboratory con-
ditions. More specifically, these variables include:

a. The study of the area-to-volume ratio effect on the rate of corro-
sion.
b. The effect of pH of water.
c. The role of dissolved oxygen in corrosion.
d. The effects of free and combined residual chlorine.
e. The impact of natural color on corrosion.
f. Alkalinity.
g. Chloride ion.
h. Sulfate ion.
i. Calcium ion.
j. Magnesium ion.
k. Sodium ion.

l. Conductivity.

m. Electrode potential, $E_H^\text{m}$.

n. The effect of the ratio of $\frac{\text{Cl}^- + \text{SO}_4^{2-}}{\text{Alkalinity}}$

All tests were at least duplicated, with others repeated 4 to 12 times for statistical evaluation of the results. It was hoped that this study would lead to the identification of those water quality parameters that are responsible for the premature failure of these metals in drinking waters. Once such factors are correctly identified, a corrosion index would be developed for those parameters of concern in potable water systems.
CHAPTER III
EXPERIMENTAL PROCEDURE AND ANALYSIS

Design of Testing Apparatus

Due to the time required to conduct corrosion experiments, a 48-unit magnetic stirring machine was designed to perform many experiments simultaneously. The individual sample jars were designed using clear plexiglass to fit the machine. The jars were 10.5 inches high, with an outside diameter of 5.5 inches, and having a capacity of approximately 4 liters. Both ends of the jars were sealed using same quality plexiglass sheet. Eight circular holes, each 0.75 inches in diameter were drilled in the top of the jar, to allow the entry of probes and coupons and to serve as inlets and outlets for gases. Figure 16 shows a schematic diagram of the sample jar. A larger hole, 1.75 inches in diameter, was centered at the top of the jar to provide entry for various probes for the in situ monitoring of the system. A 0.75 inch circular hole was also placed at a distance of 1.5 inches above the base of the jar for periodic sampling of the water for analysis. A diagram of the complete system is presented in Fig. 17.

Preparation of Corrosion Coupons

Both mild steel and copper coupons were prepared in accordance with the NACE* standard Tm-01-69 (laboratory corrosion testing of metals for the process industries) with some modifications to improve the testing conditions, and minimize the crevice and local cell effects on the rate of corrosion of the metals (237).

*National Association of Corrosion Engineers.
Fig. 16. Schematic Diagram of the Test Jar  (A) Front View  (B) Top View
Fig. 17. Diagram of the Testing Apparatus. D = Deionized Water; F = Glass Wool Filter; J = Testing Jars.
The coupons were embedded in epoxy except for the one face to be exposed. An acrylic rod was mounted on the epoxy on the back of the coupon for the purpose of handling and immersion of the specimens in the solution (Fig. 18). The mild steel coupons were cut from a 1/8 inch thick, hot-rolled sheet, while copper specimens were made from a copper sheet that had a thickness of 1/16 of an inch. The mild steel coupons were first sanded with No. 60 abrasive paper, and then polished with No. 120 grit paper to eliminate any surface irregularities. Each coupon was then examined under a magnifying glass to find out if any visible crevices existed around the edges. If crevices were noticed, they were covered using a silicone sealant. Both mild steel and copper coupons were numbered on the back with an electric engraver for identification. Galvanized steel coupons were stamped with numbers near one end of the specimens. Copper coupons were polished with No. 120 abrasive paper first, followed with a No. 600 grit paper.

Galvanized steel coupons were cut from a 3/4 inch diameter galvanized pipe, which is used for plumbing purposes. The pipes were cut into 1 1/2 inch long sections, which were then split into halves lengthwise. The galvanized steel specimens were suspended in test solutions using a thin nylon string attached to a 1/16 inch hole drilled at one end of each coupon (Fig. 19). Unlike mild steel and copper, galvanized coupons were not polished.

All coupons (mild steel, galvanized steel and copper) were degreased using Bonami* (a bleach-free polishing cleanser) followed by a thorough washing with tap water and then rinsed with distilled water.

* A product of Faultless Starch/Bon Ami Co., Kansas City, MO. 64101
The coupons were finally rinsed with acetone, air dried and stored in a desiccator. The specimens were weighed to the nearest 0.1 mg using an analytical balance. In case of mild steel and copper coupons, all edges were coated with Microshield* to cover any possible crevices that may be present at the metal-epoxy interface. The galvanized steel coupons were all coated with Microshield, except a one square inch portion of the interior surface that was to be exposed to the water. Two applications of Microshield coatings were used to eliminate any holidays. The exposed areas of all coupons were then measured and the specimens stored in a desiccator before immersion into the test solutions. The coupons were used for calculating the rates of corrosion by

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Fig. 18. Steel or Copper Coupon (A) Exposed Surface (B) Section

* A product of Tobler Division, Michigan Chrome and Chemical Co.
the weight loss method. The Magna Corrator, Model 1120* was employed for monitoring corrosion rates by electrochemical means (238). The three-electrode probes required for the determination of corrosion rates by the Corrator were constructed at the machine shop of the Department of Environmental Engineering Sciences. The copper and mild steel electrodes were also made at the same machine shop. The coupons embedded in epoxy were found to absorb and retain some moisture after exposure to the test solutions. The moisture was driven off by placing the coupons in a 105° C oven for 30 minutes.

![Fig. 19. Galvanized Steel Coupon (A) Galvanized Steel Pipe (B) Prepared Coupon L = 30 mm, w = 22 mm, d = 3/4 inch.](image_url)

* A product of Magna Instruments, a Division of Rohrback Corporation, 1186 East Telegraph Road, Santa Fe Springs, California 90670.
Synthetic Water Solutions and Chemical Reagents

All aqueous solutions were prepared using analytical reagent grade chemicals and deionized water. In the formulation of synthetic water solutions some difficulty was experienced with the use of certain chemical reagents, particularly those having lower solubilities in aqueous solutions. The glassware and plastic bottles used for preparation and handling of chemicals were washed with detergent and rinsed thoroughly with tap water and then deionized water. The containers were then soaked in a 50 percent acid bath containing both HNO₃ and hydrochloric acid. After removal from the acid solution, the bottles were washed thoroughly with tap water and then rinsed with deionized water. They were then dried and stored in clean drawers before they were used for storage of samples or reagents.

A combination of several chemicals including CaCl₂ · 2H₂O, MgSO₄ · 7H₂O, NaHCO₃, NaCl, Na₂SO₄, CaSO₄, NaOH, and MgCl₂ · 6H₂O were used to give the intended ionic composition of the test waters. Fresh stock solutions of the chemicals were prepared in accordance with the procedures described in Standard Methods (111), and then diluted with deionized water to give the desired concentration.

Preliminary Immersion Tests

Prior to the start of the main experiments, preliminary tests were conducted to determine whether the rates of corrosion of copper, mild steel and galvanized steel were affected by the ratio of the area of the exposed metal to the total volume of the solution, A/V.
The objectives of these tests were to determine the appropriate A/V ratio for each metal. Using several A/V ratios, the rates of corrosion were determined to be relatively independent of the area-to-volume ratios for the metals under consideration.

Laboratory Procedure

Three liters of the specified water was placed in each jar. The system was aerated or deaerated, as required, for about 4 hours before the immersion of metal coupons. The designated amounts of natural color and chlorine were than added to the jars, and the pH of each jar was adjusted using dilute NaOH or HCl solution. The water in each jar was agitated with a starhead magnetic stirrer at a constant speed of 60 RPM.

The natural color used in the experiments was obtained from Lake Weir, located near Ocala, Florida. About 50 gallons of the lake water was freeze-concentrated to a final volume of 5 gallons. The final color of the concentrate was 3800 color units on the platinum-cobalt scale. The lake water was prefilled through a 2.0 micron filter, followed by passage through a 0.8 micron filter to remove any suspended matter before concentration. The concentrated stock color solution was stored at 4°C. Although Lake Weir water was very low in mineral content (for example, the concentrations of Ca, Mg and Na were 1.6, 0.6 and 4.0 mg/l respectively), the addition of color would slightly increase the mineral content of the test solutions. Laboratory grade sodium hypochlorite (NaOCL) was used as the source of chlorine. Aeration was provided by continuous bubbling of compressed air through the solutions, while deaeration was achieved by the continuous
purging with purified nitrogen gas. The air was passed through a tightly packed glass-wool filter and then through deionized water before it was introduced into the system. This was necessary in order to remove grease or any particulate matter that may have been present in the air and to minimize the evaporation of the water in the jars.

Six or seven of the prepared coupons were then immersed in each jar and 2 or 3 of them were removed from the test solutions after designated periods of exposure. The times of exposure ranged from 2 weeks to over a year for some tests. After the coupons were removed, they were visually examined and the appearance of the corrosion products was recorded. The coupons were then cleaned from corrosion products using Bonami and a bristle brush. The specimens were then rinsed with distilled water. The Microshield was removed with acetone and then they were allowed to dry in the air. The final weights of the coupons were measured and the weight loss was converted into corrosion rate in mils per year (mpy).

In the case of the electrochemical measurement of corrosion rates, the probes (Fig. 20) with the electrodes were left in the jar throughout the exposure period. The electrodes were degreased in a manner similar to the coupons and their initial weights before immersion were measured. At the end of the test, the electrodes were removed, cleaned and reweighed. The water quality was monitored periodically. The pH of solutions and chlorine residuals in the jars were monitored daily. Other parameters, such as DO, alkalinity. Electrode potentials were measured in selected jars and daily readings were recorded.
Two water quality parameters proved difficult to maintain at constant levels for prolonged exposure times, and therefore required more frequent adjustments. Chlorine in particular was consumed rapidly in the corrosion process. The pH of solutions also fluctuated as corrosion continued and required daily adjustments. All tests were conducted at a temperature of 22 ± 2°C.

![Diagram of Corrator 3-electrode Probe](image)

**Fig. 20.** Corrator 3-electrode Probe (A) Probe with Electrodes (B) Test or Auxiliary Electrode; TE = Test Electrode, RE = Reference Electrode, AE = Auxiliary Electrode

**Corrosion Rate Measurements**

The rates of corrosion of mild steel and copper were determined using several techniques. (1) Instantaneous rates of corrosion were measured using a Model 1120 Corrator and the three-electrode Corrator probes.* (2) Corrosion rates were determined by the loss of weight of the exposed coupons after specified exposure periods. (3) The progress of corrosion was also monitored by measuring the change in

* A product of Magna Instruments, A Division of Rohrback Corporation, 1186 East Telegraph Road, Santa Fe Springs, California 90670.
the water quality and the pickup of Fe or Cu from the immersed coupons. Corrosion rates of galvanized steel were calculated from weight loss measurements only because of the difficulty of constructing galvanized steel Corrator electrodes. The leaching of Zn and Cd from the galvanized steel coupons was monitored in all test solutions.

Instantaneous rates of corrosion were measured at selected time intervals by placing a Corrator probe in each jar (Fig. 20). The three-electrode probe consisted of two identical electrodes that were made from the metal to be tested, and a stainless steel reference electrode. The Magna Model 1120 Corrator is a portable compact battery-operated instrument that applies a prescribed voltage (14 mv) to the probes immersed in an electrolyte (132, 238). The voltage causes a current to flow between anodic and cathodic sites in an electrolyte. The current-to-voltage ratio is proportional to the rate of corrosion of the metal.

In a 3-electrode system, two separate readings, one for anodic and one for cathodic polarization are required. The final rate of corrosion was computed from the readings. A system utilizing a 3-electrode probe was chosen over a 2-electrode system because of the close spacing of the reference electrode to the test electrode that reduces the "IR" drop through the solution. Three-electrode probes are preferred over 2-electrode probes in solutions of high resistivity. The pitting index, PI, of copper and mild steel were also measured. Although the pitting index measurement does not measure actual penetration rates of a metal by pitting, it provides some
information about the relative pitting tendency of a metal in a given solution. The Corrator meter is calibrated to read corrosion rate in mpy. However, this is not true in most cases, as the final rate of corrosion in mpy must be obtained by multiplying the observed Corrator readings by a proportionality factor, that is a function of both resistivity of the solution and of electrical polarization of the probe. The calculation of the proportionality factor "probe multiplier" (238:17) requires that the rate of corrosion in a given system be determined by some reliable independent means, such as weight loss method. The weight loss of the electrodes were used in the calculation of such factors.

The rates of corrosion by weight loss were computed in accordance with equation 55 as described earlier.

Analytical Equipment and Techniques

Determination of Metals

Metals analyses were performed using a Varian Techtron Model 1200 atomic adsorption spectrophotometer* (239). Most metals were analyzed by direct aspiration of the sample into the flame, but Cd was analyzed using flameless carbon rod atomization. The test samples were all acidified at the time of sampling using 1.5 ml of redistilled concentrated nitric acid (111). Acidification of the samples was necessary to keep the metal in solution and to minimize the adsorption of the metal on the walls of the containers. The samples were not pretreated because the test solutions were free from organic substance. The

* A product of Varian Techtron Pty. Ltd., Springvale, Australia
measured values of the metals represent the total soluble portion of the metal in solution. The wavelength and the conditions at which the metals were analyzed are recorded in Table 7.

All metal standards and samples were stored in polyethylene bottles. Atomic absorption spectrophotometry (AAS) is a useful instrument for determination of trace and small concentrations of many metals in aqueous solutions. The instrument consists of a hollow-cathode light source, made from the element to be analyzed; a burner

<table>
<thead>
<tr>
<th>Metal</th>
<th>Wavelength (nm)</th>
<th>Type and Condition of Flame*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>422.7</td>
<td>A-A            Reducing</td>
</tr>
<tr>
<td>Mg</td>
<td>285.2</td>
<td>A-A            Oxidizing</td>
</tr>
<tr>
<td>Na</td>
<td>589.0</td>
<td>A-A            Oxidizing</td>
</tr>
<tr>
<td>Fe</td>
<td>248.3</td>
<td>A-A            Oxidizing</td>
</tr>
<tr>
<td>Cu</td>
<td>324.8</td>
<td>A-A            Oxidizing</td>
</tr>
<tr>
<td>Zn</td>
<td>213.9</td>
<td>A-A            Oxidizing</td>
</tr>
<tr>
<td>Cd</td>
<td>228.8</td>
<td>C-R            -</td>
</tr>
</tbody>
</table>

*A-A Air-acetylene; C-R Carbon Rod

which aspirates an aqueous sample into the flame for atomization; a monochromator that isolates a selected spectral line from the cathode light beam directed through the flame; and a detector that uses photomultipliers to amplify and measure the intensity of the ultraviolet or visible light absorbed by the atoms of the metal in the sample. The hollow-cathode tube contains some helium, neon or argon gas, which is charged by applying a high voltage of about 400 v. The charged
atoms of these gases bombard the cathode, causing it to emit light at a particular wavelength that is a function of the cathode element (240).

In an aspirated sample, the atomized element absorbs the light emitted by the cathode. The amount of light absorbed by the atoms is proportional to the concentration of the metal in the test solution. In the analysis of Ca and Mg, 1 ml of lanthanum solution per 10 ml of sample was used in both samples and standard metal solutions, in order to overcome chemical interference from the presence of sulfate, phosphate, aluminum and silica (111).

For every metal analyzed, calibration curves from known standards were prepared in accordance with the Standard Methods (111) and the AAS instruction manual (239).

Flameless atomic absorption spectrophotometry uses a carbon rod atomizer instead of a flame in which the element is atomized with a controlled sequence of electrical power. A small sample of .5 μl is injected into the tube of the carbon rod where it is first dried, then ashed and finally atomized. Cadmium concentrations were determined using Varian Techtron Model 63 Carbon Rod Atomizer* (241). Carbon rod atomization is 20-500 times more sensitive than flame atomic absorption. An inert nitrogen gas with a supplementary hydrogen fuel was used. The fuel is controlled automatically and is required only for ash and atomize stages.

* A product of Varian Techtron Pty., Springvale, Australia.
pH and $E^\text{H}_\text{r}$ Measurements

All pH and redox potential, $E^\text{H}_\text{r}$, measurements were made using Orion Research Model 701 A digital pH/mv meter*. A research grade combination pH electrode (glass electrode plus a silver/silver chloride reference electrode) was employed for measuring all pH values. Electrode potential values were measured using a platinum combination electrode in conjunction with a saturated calomel reference electrode.

Since $E^\text{H}_\text{r}$ is the measure of redox potential of a system in reference to the Standard Hydrogen Electrode (SHE), the observed values were converted to the $E^\text{H}_\text{r}$ scale by adding 245 mv to the measured redox values (242). The instrument was capable of measuring redox values in the range -1999.9 to +1999.9 mv accurate to 0.1 mv, while the precision for pH measurements was 0.01 pH units over the pH range 0.00 to 13.99. pH electrodes were standardized both before and after pH measurements against a standard Ferrous-Ferric solution as described by Light (243).

Chlorine Residual Determination

Chlorine residuals were measured by amperometric titration or by the DPD (N, N-diethyl-p-phenylenediamine) method depending on the size of the sample. The use of the amperometric technique was preferred over the DPD method when ample volume of the sample was available. The amperometric titration was not a feasible method for frequent monitoring of chlorine residuals at low concentrations, because it requires

a 200 ml sample. The DPD procedure was used where the amperometric titration was impractical due to sample size limitation.

The amperometric procedure can accurately measure free available residual chlorine down to 0.01 mg/l. Furthermore, it can differentiate between monochloramine and dichloramine species. A Wallace & Tiernan Series A-790 Amperometric Titrator* was used in this study. An amperometric titrator consists of a motor and an agitator; a low resistance galvanic cell with a polarizable platinum alloy electrode and a silver/silver chloride reference electrode; a microammeter connected to the cell; a reagent pump unit and a 200 ml capacity sample container.

Amperometric titration is based on the reaction of available chlorine with a reducing agent such as phenylarsine oxide solution. A sample containing chlorine produces a current which is indicated by the microammeter needle on the calibrated scale. The flow of current is proportional to the concentration of chlorine present in the sample. When phenylarsine oxide titrant is added to the sample, it reacts with available chlorine, thereby reducing its concentration in the water. This in turn decreases the flow of the current as read by the microammeter. The titrant is added to the sample until all of the available chlorine is neutralized. The movement of the microammeter needle becomes sluggish when it approaches the end point of the titration. At the end point, the needle stops and the addition of phenylarsine oxide has no further effect on the microammeter pointer.

*A product of Pennwalt Corporation, Wallace * Tiernan Division, 25 Main Street, Belleville, New Jersey, 07109.
It should be noted that the meter reading itself is not important, but it serves as an indicator of the end point of the titration. Further details of the amperometric procedure are described elsewhere (111, 244, 245).

In the DPD method*, a colorimetric comparator kit was used. Various types of DPD tablets were added to the 10 ml sample in clear glass tubes in accordance with the manufacturers' instructions. The addition of the tablets to the samples containing chlorine, produces a color, the intensity of which is proportional to the concentration of chlorine present in the sample. The color developed in the samples was matched with the permanent DPD chlorine standards in the kit (246).

Color Measurement

Apparent color, that is, the original color of the samples without any filtration or centrifugation was measured by a spectrophotometer at a wavelength of 420 nm. A standard curve was prepared using several dilutions of a 500 color units platinum-cobalt standard, by plotting the absorbance against the concentration of the color. All color measurements were made at an adjusted pH of 7.6 and at several other pH values. The appropriate amounts of color were then added to the intended jars to give exact color concentrations of 10, 15, and 20 units at the desired pH levels. A unit of color is equivalent to the amount of color developed by 1 mg/l of platinum in the form of chloroplatinate ion (111).

* A product of LaMotte Chemical Products Co., Chestertown, Maryland 21620.
**Dissolved Oxygen, DO**

Dissolved oxygen concentrations were determined using YSI Model 54ARC dissolved oxygen meter* equipped with an automatic temperature compensator. A dissolved oxygen probe with a built-in stirrer was used for all DO measurements. The DO probe uses a polarographic sensor or electrode covered by an oxygen-permeable membrane. When the membrane electrode is immersed in a solution containing DO, the DO diffuses through the oxygen selective membrane. An external polarizing voltage of 0.8 V is applied across the sensor that reacts with the diffused oxygen and produces a current that is proportional to the concentration of oxygen in solution. The instrument is capable of measuring DO with an accuracy of ± 0.1 ppm on a 0-10 ppm scale (111, 247).

**Chloride Analysis**

Chloride ion concentration was analyzed colorimetrically using a Technicon Auto Analyzer*. The Auto Analyzer (AA) method was used because of its capability of handling larger numbers of samples with relative ease. An Auto Analyzer consists of a sampler; a manifold (one for each specific ion); a proportioning pump; a colorimeter and a recorder. The Ferrocyanide AAII method as described in EPA Methods for Chemical Analysis of Water and Wastes (248) was used for all chloride determinations. A color solution made of mercuric thiocyanate, Hg(SCN)$_2$; and ferric nitrate is employed in this technique. If chloride is present in a sample, it reacts with mercury and allows a colored ferric thiocyanate compound to form. The intensity of the color is proportional

* A product of Yellow Springs Instruments Co., Inc. Yellow Springs, Ohio, 45387.
* A product of Technicon Instruments Corporation, Tarrytown, New York 10591.
to the concentration of chloride in the sample. A calibration curve was constructed for each set of chloride analyses in which the peak heights of the known standards are plotted against concentrations. The concentrations of chloride in the samples were obtained by comparing their peak heights with the standard curve.

**Sulfate Analysis**

All sulfate analyses were conducted using the automated Methylthymol Blue (MTB) colorimetric method (248). In this method, the sulfate samples are initially passed through a cation exchange column for removing multivalent metal ions from the solution to minimize interference from such ions. The sulfate samples are then allowed to react with a mixed solution of barium chloride, ethanol, methylthymol blue* \((C_{37}H_{39}N_2Na_3O_{13}S)\) and hydrochloric acid to a pH value of 2.5 - 3.0 to form barium sulfate. Both barium and MTB in the mixed solution were added in excess but at equal concentrations. The pH of the solution is then adjusted to a pH of 12.5 - 13.0 to facilitate the reaction of excess barium with MTB to form a blue color in solution. The concentration of uncomplexed MTB after the completion of reaction is monitored and is equivalent to the concentration of sulfate in the sample. A set of known sulfate standards were analyzed with each set of sulfate samples for plotting a standard curve.

**Alkalinity Measurements**

Alkalinity of each sample was measured using a potentiometric titration (111). An Orion Model 701 A digital pH/mv meter* was used for titration of alkalinity to the end point pH. The end point of

*Methylthymol blue, \((3', 3''\text{-bis-N,N-bis carboxylmethyl-amino methylthymolsulfone-phtalein pentasodium salt})\) obtained from Eastman Kodak Co., Rochester, N.Y. 14650.
titration for total alkalinity was selected at pH 4.8, while pH 8.3 was chosen for phenolphthalein alkalinity. Combination pH electrodes were used for pH measurements. The electrodes were standardized with standard buffer solutions prior to any pH measurements. The titrant used for alkalinity measurements was 0.02 N hydrochloric acid.

**Conductivity Measurements**

The conductivity of the samples was measured using a YSI Model 31 Conductivity bridge (249)*. This specific instrument was equipped with an AC bridge that consists of a voltage divider range switch; a potentiometer that is connected to a dial; an electron ray indicator tube, a function switch that selects bridge frequency; a sensitivity switch that controls the sensitivity of electron ray tube; a range switch for selecting a multiplier for direct measurement of resistance or conductance; a drive control that drives dial and potentiometer and a conductivity cell made of platinized platinum-iridium electrodes.

Both resistance and conductance of a sample can be measured with this instrument. The conductivity of a sample is obtained by multiplying the conductance value in micromhos/cm by the cell constant, K. The cell constant, K, is a factor determined by the geometry of the cell and the electrodes. The cell constant was calibrated using a 0.01 M KCl solution prior to conductivity measurements. The conductivity of most U.S. drinking waters lies in the range 50-1500 micromhos/cm.

* A product of Yellow Spring Instruments Co., Inc., Yellow Springs, Ohio 45387.
CHAPTER FOUR
EXPERIMENTAL RESULTS AND DISCUSSION

Mild Steel

Many experiments were conducted to evaluate the rate of corrosion of steel under various conditions. A description of the results as affected by the water quality parameters is presented below.

Effects of Water Quality on Corrosion:

The effects of the chemical composition of water on the rate of corrosion of mild steel is presented in Figure 21. The rate of corrosion of steel was found to be higher in Water A (Table 8), than in either Water B or C.

Table 8. Chemical Composition of Synthetic Waters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca^{2+}</td>
<td>20</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>6</td>
<td>12</td>
<td>18</td>
</tr>
<tr>
<td>Na^{+}</td>
<td>23</td>
<td>46</td>
<td>69</td>
</tr>
<tr>
<td>Cl^{-}</td>
<td>36</td>
<td>71</td>
<td>107</td>
</tr>
<tr>
<td>SO_{4}^{2-}</td>
<td>24</td>
<td>48</td>
<td>72</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>50</td>
<td>100</td>
<td>150</td>
</tr>
<tr>
<td>Total Hardness</td>
<td>75</td>
<td>150</td>
<td>225</td>
</tr>
</tbody>
</table>

* All values expressed in mg/l except alkalinity and total hardness which are expressed in mg/l as CaCO_{3}.
Fig. 21. Effect of Chemical Composition of Aerated Water on the Rate of Corrosion of Mild Steel. pH 8.00, Chlorine Residual 1.50 mg/l, color 20 units.
From the data presented in Figure 21, it may be concluded that the chemical quality of water plays a major role in its corrosiveness towards a given metal.

It should be pointed out that in most of the tests conducted, the initial rates of corrosion were often higher in hard waters than in soft waters. This may have been due to higher electrical conductivity of the hard water which would influence the initiation of the attack. As the corrosion continued, the hard waters exhibited a lower rate of attack due to precipitation of both calcium carbonate and other corrosion products.

It was also observed that the corrosion product was more firmly attached to the corroding metal in hard waters than in soft waters. The differences in the rates of corrosion of a metal in waters of different chemical qualities can be explained in a number of ways. The difference in the mineral content of the waters, the concentration and type of ions, the buffering capacity of the water, dissolved oxygen, redox potential and pH all play important roles in both initiation and continuation of corrosion.

The buffering capacity of water, as described by Stumm (180) affects corrosion. Stumm's suggestion is in line with the corrosion results obtained in this study (Fig. 21). The effect of buffer capacity of water on the corrosion of a metal can be understood better if one considers the aqueous chemistry of a corroding metal surface at near neutral pH conditions.

Since the reduction of oxygen is the main cathodic reaction in the corrosion by most drinking waters (Eq. 42), the buffering capacity
of the water tends to minimize the change in pH,
\[
H_2O + \frac{1}{2} O_2 + 2e = 2OH^-
\]  (42)

The buffer intensity thus interferes directly with the formation of hydroxyl ions by the cathodic reaction. The higher the buffering capacity of a water, the greater its inhibitory effect on the rate of corrosion.

Another factor of significance is the solubility of chemical species in solution. A water of higher mineral content tends to precipitate some chemical constituents more readily than waters that are low in such minerals. The inhibitory action of the precipitation of calcium carbonate, for example, has been well documented as detailed by Merrill and Sanks (250) and others (126, 251). Chloride and sulfate ions have been shown to accelerate the rate of corrosion, while carbonate, hydroxyl, phosphate and silicate tend to form insoluble compounds that are adsorbed or deposited on the metal surface and thus impede the rate of attack.

**Effect of Exposure Time:**

Several experiments, ranging from two weeks to six months of immersion, were conducted on mild steel to evaluate the effect of exposure time on the rate of corrosion. The progress of corrosion of steel as affected by exposure time in aerated water A is presented in Fig. 22. The rate of corrosion was found to decrease from a very high initial rate to a lower, more stable rate after about 3 weeks exposure time. The same effects were observed in waters B and C. The rate of corrosion tended to increase slightly after three months exposure time,
Fig. 22. The Rate of Corrosion of Mild Steel in Soft Water (A) at Room Temperature, pH 8.00. No color or Chlorine added.
primarily due to a continuous supply of oxygen throughout the test period. Fig. 23 indicates the effects of exposure time on the rate of corrosion of mild steel in both air-saturated and deaerated soft water. The rates of corrosion were substantially higher in the 10-day exposure tests than in the 81 day exposure tests. Similar time-rate effects have been reported by other investigators (126, 251).

**Effect of pH**

The pH of water alone has little effect on the rate of corrosion of steel in the pH range 6-9.5, the pH range of most drinking waters. The effect of pH on the rate of corrosion of mild steel is presented in Fig. 23. The rate of corrosion is relatively independent of pH and decreases with increasing exposure time in both aerated and deaerated systems. Corrosion rates at pH 6.0 and 9.5 were slightly higher compared to other intermediate pH values.

Other investigators (108, 167, 252) have reported similar effects at these pH values. In drinking water, the pH of water alone may not be a significant factor in terms of reducing or enhancing corrosion reactions. The presence of other ions in water, as well as gases, are the key factors in corrosion reactions.

For example, in one set of tests, it was found that mild steel specimens did not show any signs of corrosion in aerated sodium hydroxide solutions at concentrations ranging from 10 to 160 mg/l as hydroxyl ions, the pH ranged from 10.8 to 11.7. These tests were conducted for an exposure period of two weeks.

However, increased rates of corrosion were observed at pH values similar to those of sodium hydroxide solutions when mild steel coupons
Fig. 23. Effect of pH on the Rate of Corrosion of Mild Steel at Different Exposure Times.

- □ - □ 10 days, Aerated
- □ - □ 81 days, Aerated
- □ - □ 10 days, Deaerated
- □ - □ 81 days, Deaerated
were immersed in aerated sodium bicarbonate solutions during a two weeks period. It should be noted that although pH alone may not be the primary factor in initiating the corrosion attack, its secondary effect on the solubility and speciation of metal ions cannot be over-emphasized.

Dissolved Oxygen:

The effect of dissolved oxygen on the extent of corrosion of mild steel in an air-saturated system (water A, Table 8), compared to a deaerated system is presented in Fig. 24. As can be seen, the presence of dissolved oxygen in the water is a key factor. The rate of corrosion in the deaerated system may have been even lower than that shown in Fig. 24, had all the dissolved oxygen been removed from the nitrogen-purged system. Dissolved oxygen concentrations as high as 0.5 mg/l were recorded during the exposure period in some deaerated systems. Complete deoxygenation of the systems proved to be difficult experimentally. However, the concentrations of dissolved oxygen in subsequent tests were reduced to 0.1-0.2 mg/l by increasing the flow rate of purified nitrogen gas through the test solutions.

Dissolved oxygen in water has long been recognized as one of the most potent corrosive agents to ferrous materials. As presented in Fig. 24, the rate of corrosion of mild steel in air saturated soft water was found to be much higher than in the same water deaerated. Other tests conducted on hard waters showed similar effects, that is, the rates of corrosion were significantly lower in deaerated solutions compared to those containing dissolved oxygen.
Fig. 24. Effect of Dissolved Oxygen on the Rate of Corrosion of Mild Steel in Soft Water. pH 7.00, No Color or Chlorine Added.
Dissolved oxygen in water can influence the rates of corrosion of a metal in various ways. Dissolved oxygen removes the polarizing layer of hydrogen gas from the metal surface, and exposes the metal to the electrolyte. In the absence of oxygen, the hydrogen film would decrease the current flow and hence reduce the rate of metal dissolution. Oxygen can also serve as an electron acceptor and thus be reduced to hydroxyl ions, therefore, favoring the oxidation of the metal.

Larson (164, 165) showed that dissolved oxygen exerts a dual effect on the corrosion of steel. It may accelerate or inhibit the rate of corrosion depending on the mineral quality of the water. Gilroy and Mayne (253) concluded that dissolved oxygen retarded the breakdown of air-formed passive films on iron surfaces in the pH range 6-9, by either oxidation of the ferrous ions that are present in the passive film, or by ennobling of the redox potential of iron to an extent that ferric oxide predominates.

In deaerated systems, a uniform, thin, black passive film was formed on the exposed surface of steel specimens, most probably magnetite, Fe$_3$O$_4$. In aerated systems, several uneven layers of corrosion products were formed on the metal surface. A black layer of precipitate existed adjacent to the surface. This layer was covered with a thick layer of yellowish, gelatinous, hydrated ferric oxide. The uneven precipitation of the hydrated oxides on the metal surface formed a partial diffusion barrier for the transport of oxygen to the metal surface. This may explain the fact that corrosion rates decreased with increasing exposure time.
It may be concluded that the formation of uniform corrosion products on the metal surface, as in deaerated systems, isolates the metal from the solution and hence reduces the rate of corrosion drastically. On the other hand, the formation of uneven films on the metal surface as in air-saturated systems, may lead to enhanced corrosion due to the formation of local concentration cells. It should be pointed out that uneven distribution of the corrosion product on the metal surface also affects the ratio of the area of anode to cathode. This may lead to increased localized corrosion in unprotected anodic sites at the expense of protection of the cathodic areas.

The mechanism of formation of these films has been discussed by Morris (254) and Sato (255). In the absence of oxygen, Morris (254) described the mechanism of corrosion of iron as the diffusion of both ferrous ions and electrons through a thin film of magnetite, with hydrogen production as the rate controlling factor. These reactions are shown as:

\[ \text{Fe} = \text{Fe}^{++} + 2e \]  \hspace{1cm} (27)
\[ 2\text{H}_2\text{O} + 2e = 2\text{OH}^- + \text{H}_2 \]  \hspace{1cm} (65)
\[ 3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2 \]  \hspace{1cm} (66)

The magnetite film was shown to be 8-15 Å in thickness. In the presence of dissolved oxygen, a thin film of magnetite is formed initially which can be oxidized to $\gamma$-Fe$_2$O$_3$. Iron continues to dissolve and enter solution as ferrous ions which are oxidized to hydrated ferric oxide (FeOOH) by dissolved oxygen. Since hydrated
ferric oxide is highly insoluble in water, it precipitates on the metal surface and restricts the flow of oxygen to the metal surface.

\[
3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2 \tag{66}
\]

\[
\frac{1}{2} \text{O}_2 + 2\text{Fe}_3\text{O}_4 = 3\text{Fe}_2\text{O}_3 \tag{67}
\]

\[
2\text{Fe}^{++} + \frac{3}{2} \text{O}_2 + \text{H}_2\text{O} + 4\text{e} = 2\text{FeOOH} \tag{68}
\]

Morris (254) also suggested that the passive film on an iron surface in the presence of dissolved oxygen and buffering reagents such as sodium carbonate is primarily $\gamma$-$\text{Fe}_2\text{O}_3$ with some hydrated oxide.

Walker et al. (153) indicated that the rate of corrosion of steel in an aqueous solution was a linear function of the oxygen content of the water. Cox and Roetheli (155) showed that a linear relationship between dissolved oxygen and the rate of corrosion of steel was maintained if dissolved oxygen concentrations were 9 mg/l or less. Beyond 9 mg/l dissolved oxygen, a lower rate of corrosion was noted. Stumm and Lee (256) showed that both oxygen and pH play a significant role in the oxidation of ferrous iron to the ferric form. An increase in pH was shown to strongly influence the rate of oxygenation of ferrous iron.

**Chlorine Residual:**

The effect of chlorine residual on the rate of corrosion of mild steel is presented in Fig. 25. It shows that the presence of 1.5 mg/l free chlorine residual had a positive effect on the rate of corrosion of mild steel in both aerated and deaerated solutions.

Difficulties were encountered in maintaining a constant chlorine residual throughout the test period. Chlorine had to be added to the
Fig. 25. Effect of Chlorine Residual on the Rate of Corrosion of Mild Steel in Hard Water. pH 8.00; No Color Added

- ○ ○ Chlorine = 1.50 mg/l
- □----□ Chlorine = 0.00 mg/l
test solutions periodically. The instability of chlorine in water for prolonged times is indicative of its tendency to take part in corrosion reactions. Chlorine as a strong oxidizing agent is reduced to chloride ion. Its reduction promotes the oxidation of the metal.

Chlorine can accelerate the rate of attack of iron by either direct increase of the redox potential of the electrolyte that favors the dissolution of iron to ferrous and then ferric ions, or through a sequence of chemical reactions that produce hydrogen ions, hypochlorous acid, hypochlorite ions and chloride as shown below:

\[
\begin{align*}
\text{Cl}_2 + 2\text{H}_2\text{O} &= \text{H}^+ + \text{Cl}^- + \text{HOCl} \\
\text{HOCl} &= \text{H}^+ + \text{OCl}^-
\end{align*}
\]

Volkening (166) showed that chlorine dosage in the range of 0-4 mg/l increased the rate of corrosion of mild steel in seawater. Similar effects of chlorine were reported by Larson (257). Larson noted that the rate of corrosion of steel increased when free chlorine concentration was 0.4 mg/l or greater. Combined chlorine in the form of \(\text{NH}_2\text{Cl}\) was shown to exert an inhibiting effect on the rate of corrosion of steel when present at concentrations of 0.4-3.6 ppm as Cl\(_2\) (126).

The effect of chlorine, like that of oxygen, diminishes after the corroding surface is passivated with corrosion by-products.

**Natural Color:**

The presence of natural color at levels of 0, 15, and 20 platinum-cobalt units (PCU) on the corrosion of mild steel was evaluated in a series of experiments. It was found that increasing color had a negative effect on the rate of corrosion of steel (Fig. 26). Furthermore, it was observed that most of the color was coagulated and was removed from solution by corrosion products.
Fig. 26. Effect of Color on the Corrosion of Mild Steel in Hard Water, pH 8.00. Chlorine Residual 1.00 mg/l

○ No Color
△ 15 Color Units
□ 20 Color Units
Larson (187) reported a significant decrease in the rate of corrosion of cast iron specimens in the presence of 2 PCU of extracted color in a limited number of tests. The large difference in the color tests may be due to the type and the nature of the color. According to Christman and Ghassemi (258), organic color in natural waters is comprised of complex polynuclear molecules derived from decayed natural plants, and has acidic properties. Color has an average molecular weight of 456.

**Effect of Specific Ions**

Although most drinking waters contain the major cations and anions, their concentrations vary greatly from one supply to another. Several experiments were conducted to evaluate the effect of specific ions such as chloride, sulfate, bicarbonate and their associated cations on the corrosion of mild steel. The findings of these tests are summarized below.

**Chloride ions**

A number of short-term experiments were conducted on the corrosion of mild steel. Three chemical compounds containing chloride (NaCl, CaCl$_2$.2H$_2$O and MgCl$_2$.6H$_2$O) were tested at four different concentrations, ranging from 10 mg/l to 160 mg/l of chloride ion. Both weight loss and Corrator probes were used to measure the rates of corrosion. The pH in some of the tests was adjusted to 8.40 using a sodium borate buffer, while no attempt was made to adjust the pH in others. All tests were aerated. The results of the chloride tests are summarized in Figs. 27 and 28.
Fig. 27. Effect of Chloride on the Rate of Corrosion of Mild Steel at pH 8.40. A, B, C Weight Loss. D, E, F Corrator. A, D NaCl; B, E CaCl₂; C, F MgCl₂.

- ○ 10 mg/l Cl⁻
- ■ 100 mg/l Cl⁻
- ● 50 mg/l Cl⁻
- □ 160 mg/l Cl⁻
The rates of corrosion of mild steel increased with increasing concentrations of chloride ion, and were generally not affected by the type of cation. The rates, however, were somewhat higher in unbuffered solutions compared to those to which sodium borate was added as a buffer.

The corrosion rates as determined by the two methods were generally in good agreement. The mechanism of corrosion by chloride ion has been well documented elsewhere (81, 187). The point to be made here is that in the presence of oxygen, the ferrous ion is oxidized to ferric hydroxide. This results in the formation of hydrochloric acid in accordance to the following chemical reactions:

Anode:

(a) \[ \text{Fe} = \text{Fe}^{++} + 2e \]  
(b) \[ \text{Fe}^{++} + 2\text{Cl}^- = \text{FeCl}_2 \]  
(c) \[ 2\text{FeCl}_2 + 5\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 = 2\text{Fe(OH)}_3 + 4\text{HCl} \]

Cathode:

(a) \[ \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2e = 2\text{OH}^- \]  
(b) \[ 2\text{H}_2\text{O} + 2e = \text{H}_2 + 2\text{OH}^- \]  
(c) \[ 2\text{Na}^+ + 2\text{H}_2\text{O} + 2e^- = 2\text{NaOH} + \text{H}_2 \]  
(d) \[ \text{Ca}^{++} + 2\text{H}_2\text{O} + 2e = \text{Ca(OH)}_2 + \text{H}_2 \]  
(e) \[ \text{Mg}^{++} + 2\text{H}_2\text{O} + 2e = \text{Mg(OH)}_2 + \text{H}_2 \]

The aggressivity of chloride ion is largely due to its ability to form soluble ferrous compounds and thus generate hydrogen ions by reaction with water. This lowers the pH at the anode. This differential in pH between the anode and the cathode promotes the rate of corrosion by causing a potential gradient between the anodic and cathodic sites.
Fig. 28. Effect of Chloride ion on the Rate of Corrosion of Mild Steel in Aerated Solutions. pH 7.18, Exposure Time 11 Days

Equations 72-74 present the reactions at the cathode caused by the salts of NaCl, CaCl₂ and MgCl₂ respectively. The right side of equations 72-74 would raise the pH at the cathode, thus causing a further increase in the rate of corrosion.

Chloride ion has been particularly noted for the breakdown of passivity in many ferrous alloys and it is considered as one of the main causes of pitting in stainless steels (259). Similar results were reported by Hatch and Rice (173), that is, increasing chloride concentrations had a positive effect on the rate of corrosion of steel.
Table 9. Effect of Chloride and Sulfate on Rate of Corrosion of Steel in mpy at pH 8.40 Weight Loss Method

<table>
<thead>
<tr>
<th>No.</th>
<th>Chemical Compound</th>
<th>Cl(^-) or SO(_4^{2-}) mg/l</th>
<th>Corrosion Rate, mpy 4 days 11 days 25 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaCl</td>
<td>10</td>
<td>5.9  4.5  8.9</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>50</td>
<td>13.4 9.7  10.5</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>100</td>
<td>16.0 11.1 11.6</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>160</td>
<td>19.3 11.2 12.4</td>
</tr>
<tr>
<td>5</td>
<td>CaCl(_2).2H(_2)O</td>
<td>10</td>
<td>4.3  4.0  5.1</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>50</td>
<td>13.2 10.2 10.3</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>100</td>
<td>17.2 12.7 9.4</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>160</td>
<td>19.6 14.8 12.5</td>
</tr>
<tr>
<td>9</td>
<td>MgCl(_2).6H(_2)O</td>
<td>10</td>
<td>6.2  5.2  8.3</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>50</td>
<td>13.0 11.3 10.7</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>100</td>
<td>15.7 12.4 12.1</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>160</td>
<td>16.5 13.3 13.7</td>
</tr>
<tr>
<td>13</td>
<td>NaSO(_4)</td>
<td>10</td>
<td>13.4 9.0  11.8</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>50</td>
<td>13.4 10.1 10.7</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>100</td>
<td>14.3 12.5 12.6</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td>160</td>
<td>18.2 13.0 12.9</td>
</tr>
<tr>
<td>17</td>
<td>CaSO(_4)</td>
<td>10</td>
<td>10.4 9.0  10.5</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td>50</td>
<td>12.9 9.7  11.0</td>
</tr>
<tr>
<td>19</td>
<td></td>
<td>100</td>
<td>14.5 11.0 10.7</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>160</td>
<td>14.6 12.0 13.1</td>
</tr>
<tr>
<td>21</td>
<td>MgSO(_4).7H(_2)O</td>
<td>10</td>
<td>14.2 10.1 11.7</td>
</tr>
<tr>
<td>22</td>
<td></td>
<td>50</td>
<td>15.2 11.2 11.9</td>
</tr>
<tr>
<td>23</td>
<td></td>
<td>100</td>
<td>17.4 12.8 14.1</td>
</tr>
<tr>
<td>24</td>
<td></td>
<td>160</td>
<td>19.5 13.5 15.0</td>
</tr>
</tbody>
</table>
Sulfate ions

The effect of sulfate ion on the rate of corrosion of mild steel was investigated using three different sulfate salts (Na₂SO₄, CaSO₄, and MgSO₄·7H₂O). The pH of the sulfate solutions and the concentration of sulfate ions were similar to those of the chloride tests. The rates of corrosion of steel, as affected by sulfate ion, are presented in Figs. 29 and 30. The average rates of corrosion of steel in both chloride and sulfate solutions are included in Table 9.

In a separate series of tests, the concentrations of chloride, or sulfate ions were established at 10, 50, 100 and 160 mg/l as in previous tests, but the solution contained all three cations Na⁺, Ca²⁺ and Mg²⁺. The resulting rates of corrosion are summarized in Fig. 31 and Table 10. The rates of corrosion of steel were not affected by any of the cations studied. The corrosion rates as determined by the weight loss and Corrator methods were found to be generally in good agreement. As can be seen, the rates of corrosion increased with increasing concentrations of both chloride and sulfate ions. The mechanism of the increased rate of corrosion of iron by sulfate ions is similar to that of chloride ions. In the absence of dissolved oxygen, the anode will contain ferrous sulfate and ferrous hydroxide. When dissolved oxygen is present, the ferrous ion is oxidized to ferric hydroxide and sulfuric acid is formed (187). The production of H₂SO₄ (Eqs. 75-78) will lower the pH at the anode, while the pH at the cathode would be increased by the cathodic reactions (Eqs. 71-74).
Fig. 29. Effect of Sulfate on the Rate of Corrosion of Mild Steel at pH 8.40. A, B, C Weight Loss. D, E, F Corrator. A, D Na$_2$SO$_4$; B, E CaSO$_4$; C, F MgSO$_4$.

- ○ ○ 10 mg/l SO$_4$$^-$
- ■ ■ 100 mg/l SO$_4$$^-$
- ● ● 50 mg/l SO$_4$$^-$
- □ □ 160 mg/l SO$_4$$^-$
Fig. 30 Effect of Sulfate Ion on the Rate of Corrosion of Mild Steel in Aerated Solutions. pH = 7.23, Exposure Time 11 days

Table 10. Average Rate of Corrosion of Mild Steel in Chloride and Sulfate Solutions.

<table>
<thead>
<tr>
<th>Chemical Compounds</th>
<th>Anion Concentration (mg/l)</th>
<th>Corrosion Rate, mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4 days</td>
<td>11 days</td>
</tr>
<tr>
<td>NaCl + CaCl₂·2H₂O</td>
<td>10</td>
<td>6.6</td>
</tr>
<tr>
<td>+ MgCl₂·6H₂O</td>
<td>50</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>15.3</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>18.0</td>
</tr>
<tr>
<td>Na₂SO₄ + CaSO₄</td>
<td>10</td>
<td>12.4</td>
</tr>
<tr>
<td>+ MgSO₄·7H₂O</td>
<td>50</td>
<td>13.3</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>15.6</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>19.8</td>
</tr>
</tbody>
</table>
Fig. 31. Effect of Chloride and Sulfate on the Rate of Corrosion of Mild Steel in Aerated Solutions Containing Ca^{++}, Mg^{++} and Na^{+} ions. pH 7.28

This difference in pH would increase the redox potential which would result in the accelerated rate of attack of steel specimens.

\[
\begin{align*}
\text{Fe} &= \text{Fe}^{++} + 2e \\
\text{Fe}^{++} + 20\text{H}^- &= \text{Fe(OH)}_2 \\
\text{Fe}^{++} + \text{SO}_4^{=} &= \text{FeSO}_4 \\
2\text{FeSO}_4 + 5\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 &= 2\text{Fe(OH)}_3 + 2\text{H}_2\text{SO}_4
\end{align*}
\]
In a 5 day test, Hatch and Rice (173) showed that the rate of corrosion of steel in sulfate solutions was substantially higher than in chloride solutions of same anion concentrations.

**Bicarbonate ions**

Two types of experiments were designed to evaluate the effect of alkalinity on the rate of corrosion of mild steel. In one set of experiments, the test solutions were composed of variable amounts of $\text{Cl}^-$, $\text{SO}_4^{2-}$, $\text{Na}^+$, $\text{Ca}^{++}$ and $\text{Mg}^{++}$ ions with different alkalinity levels. In another series of tests, different concentrations of sodium bicarbonate were tested. The effects of alkalinity on the rate of corrosion of mild steel are presented in Figs. 32-33 and Tables 11-12.

It is interesting to note that alkalinity reduced the rates of corrosion of mild steel in waters containing other cations and anions, while the rates of corrosion increased progressively with increasing sodium bicarbonate concentrations when other ions were absent. The lower rates of corrosion in the former could probably be attributed to the interaction among cations and anions, particularly calcium and carbonate. The higher rates of corrosion at high sodium bicarbonate solutions (Table 12) are mainly due to the conductivity effects. In solutions containing other ions, the presence of alkalinity at 25 mg/l as CaCO$_3$ enhanced the rate of corrosion slightly, compared to those containing no alkalinity. An opposite effect was observed at sodium bicarbonate concentration of 100 ppm, that is the rates of corrosion were substantially lower at this concentration than at any other bicarbonate concentrations.
Fig. 32. Effect of Alkalinity on the Rate of Corrosion of Mild Steel in Solutions Containing Chloride and Sulfate Ions. A, B, C pH 8.20; D pH 8.60.

- **A** No Alkalinity
- **B** 25 mg/l Alkalinity as CaCO₃
- **C** 100 mg/l Alkalinity as CaCO₃
- **D** 200 mg/l Alkalinity as CaCO₃
Exposure Time, days

Fig. 33. Effect of Bicarbonate Ion on the Rate of Corrosion of Mild Steel in Aerated Solutions.

The effect of the ratio of \((\text{Cl}^- + \text{SO}_4^{2-})/\text{alkalinity}\) on the rate of corrosion of mild steel is shown in Fig. 34. The rate of corrosion appeared to increase with increasing ratio of \(\frac{\text{Cl}^- + \text{SO}_4^{2-}}{\text{Alkalinity}}\) (ratio expressed in millequivalents) beyond a ratio of 0.2.
Table 11. Effect of Alkalinity on the Rate of Corrosion of Mild Steel.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Alkalinity* (mg/l)</th>
<th>Cl⁻ (mg/l)</th>
<th>SO₄²⁻ (mg/l)</th>
<th>Corrosion Rate, mpy 4 days</th>
<th>Corrosion Rate, mpy 11 days</th>
<th>Corrosion Rate, mpy 25 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>5</td>
<td>5</td>
<td>10.5</td>
<td>7.4</td>
<td>8.9</td>
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<td>2</td>
<td>0</td>
<td>25</td>
<td>25</td>
<td>12.7</td>
<td>8.8</td>
<td>9.6</td>
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<tr>
<td>3</td>
<td>0</td>
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<td>16.0</td>
<td>10.6</td>
<td>12.1</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>80</td>
<td>80</td>
<td>21.1</td>
<td>12.6</td>
<td>13.6</td>
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<td>11.9</td>
<td>11.8</td>
</tr>
<tr>
<td>8</td>
<td>25</td>
<td>80</td>
<td>80</td>
<td>19.6</td>
<td>12.5</td>
<td>13.7</td>
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<td>5</td>
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<td>7.9</td>
<td>7.2</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>25</td>
<td>25</td>
<td>8.9</td>
<td>7.1</td>
<td>8.3</td>
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<td>100</td>
<td>50</td>
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<td>12.2</td>
<td>8.4</td>
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<tr>
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<td>100</td>
<td>80</td>
<td>80</td>
<td>15.9</td>
<td>10.8</td>
<td>9.6</td>
</tr>
<tr>
<td>13</td>
<td>200</td>
<td>5</td>
<td>5</td>
<td>4.7</td>
<td>3.1</td>
<td>8.0</td>
</tr>
<tr>
<td>14</td>
<td>200</td>
<td>25</td>
<td>25</td>
<td>8.5</td>
<td>6.9</td>
<td>9.0</td>
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<tr>
<td>15</td>
<td>200</td>
<td>50</td>
<td>50</td>
<td>12.3</td>
<td>7.2</td>
<td>10.4</td>
</tr>
</tbody>
</table>

* Alkalinity mg/l as CaCO₃ added as NaHCO₃. Each solution contains Na⁺, Ca²⁺ and Mg²⁺ ions.

Table 12. Effect of Sodium Bicarbonate on the Corrosion of Mild Steel

<table>
<thead>
<tr>
<th>Test No.</th>
<th>HCO₃⁻ (mg/l)</th>
<th>pH</th>
<th>Corrosion Rate, mpy 4 days</th>
<th>Corrosion Rate, mpy 11 days</th>
<th>Corrosion Rate, mpy 20 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>7.06</td>
<td>2.9</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>7.35</td>
<td>11.8</td>
<td>6.7</td>
<td>8.6</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>7.94</td>
<td>13.2</td>
<td>10.0</td>
<td>10.8</td>
</tr>
<tr>
<td>4</td>
<td>160</td>
<td>8.22</td>
<td>14.4</td>
<td>13.0</td>
<td>11.3</td>
</tr>
</tbody>
</table>
The effect of bicarbonate on the rate of corrosion of mild steel as opposed to chloride and sulfate ions is somewhat different, even if calcium ions are not present in solution. The major difference in the corrosion reactions between chloride, sulfate and bicarbonate ions, is that both chloride and sulfate ions corrode ferrous materials by forming HCl and H₂SO₄ at the anode, while alkalinity results in the formation
of carbonic acid. Since carbonic acid is a weak acid, it dissociates weakly, therefore its effect in lowering the pH at the anode is minimal.

When calcium is present in solution, it reacts with hydroxyl and bicarbonate ions at the cathode and precipitates insoluble calcium carbonate (216, 187). The chemical reactions are shown below:

Anode: \[ \text{Fe} = \text{Fe}^{++} + 2e \] \[ 2\text{Fe}^{++} + 5\text{H}_2\text{O} + 4\text{HCO}_3^- + \frac{1}{2}\text{O}_2 = 2\text{Fe(OH)}_3 + 4\text{H}_2\text{CO}_3 \] (80)

Cathode: \[ \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2e = 2\text{OH}^- \] \[ \text{Ca}^{++} + \text{OH}^- + \text{HCO}_3^- = \text{CaCO}_3 + \text{H}_2\text{O} \] (82)

The inhibitory effect of calcium carbonate on the corrosion of mild steel has been noted by several investigators (96–99). Hatch and Rice (173) in a series of laboratory tests demonstrated that the deposition of calcium carbonate inhibited the corrosive effects of both chloride and sulfate ions on steel specimens.

**Redox Potential:**

Redox potential is an important parameter in electrochemical corrosion. The response of a platinum electrode for measuring redox potential, \( E_H \) in a corroding system is presented in Fig. 35. This indicates that several hours were required to establish a steady state condition before an \( E_H \) value could be measured accurately.
Fig. 35. Electrode Response in a Typical Mild Steel Corrosion System. pH 8.10
The measured $E_H$ values in water B were plotted on the $E_H - pH$ diagram (Fig. 36). All measured $E_H$ values coincided with a thermodynamically passive region. This indicates that if aggressive ions such as chloride and sulfate are excluded from the solution, the metal surface will form a passive film. As long as that film is maintained, corrosion will be drastically reduced.

Electrode potential measurements in drinking waters should be interpreted with care as cautioned by Morris and Stumm (260). Some of the reasons are: (1) Most redox reactions in drinking waters are slow and may not reach the state of a reversible equilibrium. (2) Several cations, anions, and gases which are usually present in any drinking water contribute to the measured $E_H$ values. This causes the measured potentials to be mixed potentials which are difficult to quantify. (3) The measured $E_H$ values in the bulk of the solution may be entirely different from the actual $E_H$ at the surface of the corroding metal surface. (4) Corroding systems are dynamic systems at which both dissolution and precipitation reactions are taking place simultaneously.

Despite these limitations, redox potential measurement and Pourbaix (116) diagrams provide useful information for understanding the thermodynamic behavior of a given metal in an aqueous system. As Fig. 35 indicates, the $E_H$ values after immersion declined fairly rapidly during the first several hours which may suggest that, (a) redox measuring electrodes were in the process of establishing an equilibrium with the species in the solution, and (b) that the
Fig. 36. Pourbaix Diagram for $5 \times 10^{-6}$ M Fe in the Presence of 100 mg/l Alkalinity as CaCO₃, with Measured Eₜ Values. • Aerated @ Deaerated
declining $E_H$ values showed the onset of corrosion as opposed to passivation. As corrosion continued for a number of days, the $E_H$ values tended to increase gradually, indicating that passivation of the iron was taking place. The degree of passivity largely depended on the presence of oxygen, the type of passivating ions and the quality of adsorbed or deposited film on the metal surface.

In addition to $E_H$, the conductivity of selected solutions was measured during the experiments. As the conductivity of a given solution is a gross measure of the ability of that solution to conduct electrical current, it plays a major role in initiation of corrosion attacks by completing the electrical circuit in the corrosion cell. Once the metal surface is coated with impervious corrosion by-products, the role of conductivity, however, becomes minor.

The rates of corrosion increased with increasing $\text{Cl}^-$, $\text{SO}_4^{2-}$, $\text{Na}^+$ and $\text{Mg}^{++}$ ions when the solution did not contain any carbonate alkalinity. The rates of corrosion were found to be substantially lower in the presence of carbonate alkalinity, even when the solution conductivities were high.

It appears that the type of minerals present in solution are the governing factors in reducing or enhancing the rates of corrosion.

**Variation in Water Quality**

Two types of tests were performed. In one series of tests, the experimental water quality variables were frequently readjusted to their initial values, while in the other no such attempt was made. The water quality parameters were repeatedly monitored in both cases.
Of all the parameters monitored, the concentrations of Na$^+$, Mg$^{2+}$, Cl$^-$, and SO$_4^{2-}$ remained relatively constant throughout the exposure period. The pH of the solutions changed rather quickly and required frequent adjustments. The greatest instability in pH values was observed in waters of low buffer capacity and low ionic composition.

The concentrations of alkalinity and calcium ion were both affected by the exposure time under both aerated and deaerated conditions. The change in alkalinity was very pronounced in hard waters compared to soft waters. This was consistent with the experimentally determined corrosion rate values where an appreciable amount of alkalinity precipitated with calcium in hard waters. This may have been in part responsible for the lower rates of corrosion experienced in hard waters compared to those in the soft waters.

The results of the iron pickup by the solutions are shown in Fig. 37. The initial concentration of iron was 0.0 mg/l. The maximum concentrations of total soluble iron occurred after about 24 hours of exposure in all aerated waters, after which it decreased progressively as the experiments continued. This reduction in the concentration of iron could be explained in a number of ways: (1) decrease in the rate of corrosion with time, (2) precipitation of hydrated ferric oxide by reaction of dissolved iron with oxygen, and (3) lower solubility of ferric oxide.

On the other hand, the deaerated systems picked up only small quantities of iron as the result of lower rates of corrosion. The anodic reaction was stifled by the elimination of dissolved oxygen from the water.
Fig. 37. Changes in Concentration of Soluble Iron Due to the Action of Corrosion, pH 8.00.

- ■ Water A, Aerated
- ▲ Water B, Aerated
- ● Water C, Aerated
- ✗ Water A, Deaerated
- + Water B, Deaerated
- ○ Water C, Deaerated
For aerated systems at the initial stages of corrosion, waters B and C picked up more iron than water A, while this difference became minimal after two weeks of exposure. In the deaerated systems, water A picked up slightly more Fe than the hard waters, possibly due to the effect of low buffer capacity.

The Nature of Corrosion

From laboratory observations, it may be concluded that the corrosion of mild steel was usually of the "general type", covering the entire surface of the metal exposed to the solution. Occasionally, only a part of a coupon corroded preferentially, while the rest of the coupon did not show any signs of corrosion. Corrosion in such cases was also of the "general type". Some of the coupons corroded evenly, while others corroded unevenly. One reason for the absence of pitting corrosion in the tests was probably the duration of the tests. Pitting normally requires an induction period to be nucleated and a longer exposure time to propagate.

The corrosion of steel and cast iron in distribution systems is usually "general" or "localized". The latter type of corrosion, referred to as tuberculation is a type of pitting in which an active pit is covered by growing mounds of corrosion products. This reduces the pipe size and increases the roughness of the inside surface of the pipe, thereby restricting the flow of water significantly. In extreme cases of tuberculation, there is total blockage of the pipe.

The occurrence of pits is common in those metals that display active-passive transition. To understand how and why pitting takes place, a brief review of passivity is in order.
Passivity is a condition that is due to the formation of a protective film of oxide or other chemical species on the metal surface, which renders the metal more noble and therefore results in reduced corrosion. The nature and type of such films depend on the type of metal and the type of dissolved ions and gases in solutions. There is still a great deal of controversy concerning the mechanism of formation of such films and their morphology.

According to Cohen (261), there has been little change in the basic theories of passivity since they were proposed almost 150 years ago. The two basic theories of passivity are: (1) the oxide film theory, and (2) the electronic change in the metal (261). A modification of the latter theory is the adsorption theory (108), in which passivity is induced by chemisorption of oxygen on the metal surface. The formation of passive films has been suggested (261) to result from heterogeneous reactions between the metal and solution including adsorption, anodic dissolution and precipitation.

Several models have been proposed (261) for the structure of these passive films on iron surfaces as indicated in Fig. 38. The main difference among these models is attributed to the presence or absence of water or hydrogen in the films.

Fig. 38B, for example, is a modification of the cubic oxide film by including hydrogen or water in the film. Model C (Fig. 38) has been proposed in acid solutions, while Model D has been suggested in neutral solutions (261). The difference between Models C and D is the presence of γ-FeOOH, the solubility of which is affected by
Fig. 38. Proposed Models of Passive Films on Steel (261).

(A) Cubic Oxide Film.
(B) Inclusion of Water or Hydrogen in Model A.
(C) Passive Film in Acid Solutions.
(D) Passive Film in Neutral Solutions.
(E) Hydrated Polymeric Oxide Film.
(F) Cation Deficient Film.
by the pH of solution. Form E is a hydrated polymeric oxide film and model F is a cation-deficient oxide film observed in borate solutions (261).

It is believed that oxide films are semiconductors and that vacancies, hydrogen, water and the type of metal and solution play important roles in the morphology and modification of such films (258, 261).

Pitting is caused by the local breakdown of passive films. Greene and Fontana (178), in a critical review of pitting concluded that Cl\(^-\), Br\(^-\) and ClO\(_4^-\) are the most important anions that cause pitting. They further noted that oxidizing metal halides, such as Ferric, cupric and mercuric halides caused more pitting than non-oxidizing metal halides, such as calcium, aluminum, and sodium halides. Kolotyrkin (262), listed several other factors that cause pitting, in addition to ones described by Greene and Fontana (178). Bromide ion and dissolved oxygen in the presence of halide ions were mentioned. Other factors included the structure and physical state of the metal surface, the rate of diffusion of aggressive anions, the extent and conditions of cathodic reactions, and the anode-cathode area ratio (262).

With regard to the theories of pitting, Kolotyrkin (262) concluded that: (1) pits are formed at the anodic sites, primarily due to increased acidity at the anode, and (2) that pits are caused by the displacement of passivating dissolved oxygen by aggressive anions.

Galvele (263) on the other hand presented several theories of pitting, namely: (1) oxide film defects on the metal surface,
(2) ion migration and contamination of the oxide film, (3) competitive adsorption between passivating and non-passivating species, (4) critical concentration of aggressive anions, (5) salt film formation on the metal surface, and (6) localized acidification of the metal that interferes with the repair of the passive films. Galvele (263) further emphasized the significance of pitting potential*, the role of nucleation sites such as sulfide and other non-metallic inclusions, and the effect of alloying elements.

The effect of aggressive ion concentration on the lowering of pitting potential, $E_p$, was reported by Galvele (263) to have the following relation (Eq. 83):

$$E_p = A - B \log C$$

(83)

where $A$ and $B$ are constants, and $C$ is the concentration of the aggressive anion. Galvele (263) noted that pH did not affect the pitting potential of the metal. It may be concluded that pitting occurs in two stages. Nucleation of pits on a passive surface, followed by propagation into an active pit (264, 265). Wranglen (264) noted that in carbon steels, pits initiate at the sulfide inclusions. The nucleation of pits whether due to flaws in the oxide films (263) or by competitive adsorption and displacement of passivating species (262, 263, 265) by aggressive anions, leads to the rupture of the passive films and ultimately the development of deeper pits.

* The potential above which pitting initiates on the metal surface and below which the metal remains passive.
The effect of chloride on the breakdown of passive films, and some of the reactions that make pitting possible are illustrated in Figs. 39 and 40 respectively (258, 261).

Fig. 39 shows the dual role of water in either film formation or its displacement by chloride ion. Fig. 39 A presents the metal ion that is produced anodically at a site of oxide defect, which is contained in the gel-like hydrated passive film. In the absence of chloride ion (Fig. 39 B), the dissolved metal ions form a film through bridging of OH bonds (258). When chloride is present in solution, it interferes with the bridging action by replacing water molecules (Fig. 39 C).

The film is finally ruptured by the penetration of chloride ion resulting in release of dissolved metal ions (Fig. 39 D).

The general reactions (Eqs. 84-89) involved in the breakdown of passive films as described by Cohen (261) are summarized in Fig. 40.

\[
\begin{align*}
\text{Fe} + \text{H}_2\text{O} &= \text{FeOH}^+ + \text{H}^+ + 2\text{e} \\
4\text{FeOH}^+ + 8\text{Cl}^- + 4\text{H}_2\text{O} &= 4\text{FeOOH} + 8\text{HCl} + 4\text{e} \\
\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} + 2\text{e} &= 2\text{Fe}^{++} + 6\text{OH}^- \\
\text{FeOOH} + \text{H}_2\text{O} + \text{e} &= \text{Fe}^{++} + 3\text{OH}^- \\
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} &= 4\text{OH}^- \\
2\text{H} + 2\text{e} &= \text{H}_2
\end{align*}
\]

Cohen (261) states that reaction 84 takes place at sites of oxide defects at B and C on the passive metal, thus initiating the corrosion. The possible repair of the passive film is caused by reaction 85. Reactions 86 and 87 are the key reactions that remove the oxide.
Fig. 39. Schematic Diagram of the Breakdown of Passive Film by Chloride Ions. (A) Dissolution of Metal (B) Film Formation Due to Hydrogen Bonding (C) Replacement of Water by Chloride Ions (D) Film Breakdown (258).

Fig. 40. Breakdown of Iron Film (261).
film at A, the widening of the break at B and creating a crack at site C. Equations 88 and 89 are the cathodic reactions at A that are necessary for the initiation and continuation of the anodic reactions (Eqs. 84 and 85) as summarized by Cohen (261).

When a pit forms an oxygen cell, it has just moved from its nucleation stage to that of propagation (264). The interior of the pit acts as a small anode, while its surrounding area becomes a large cathode. The pitting action continues by an "auto catalytic" (264:342) or self-generating process, because of the desirable conditions for the continuation of corrosion reactions. Wranglen (264) states that in pitting of steels, only one anodic reaction occurs (Eq. 90) as opposed to several cathodic reactions (Eq. 91-94).

Anodic reaction:

\[
\text{Fe} = \text{Fe}^{++} + 2e
\]  

(90)

Cathodic Reactions:

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e = 4\text{OH}^-
\]  

(91)

\[
\text{Fe(III) - oxide} + e = \text{Fe(II) - oxide}
\]  

(92)

\[
\text{Fe(III) - ion} + e = \text{Fe(II) - ion}
\]  

(93)

\[
2\text{H}^+ + 2e = \text{H}_2
\]  

(94)

According to Wranglen (264), reactions 91 and 92 take place outside the pit, while reaction 93 occurs at the mouth of the pit. The evolution of hydrogen (Eq. 94) takes place inside the pit.

The autocatalytic nature of pit propagation and some of the important reactions necessary for the growth of the pit (264) are presented in Fig. 41. Pit growth is assisted by a series of oxidation, reduction, hydrolysis, ion migration, diffusion and precipitation reactions that take place both inside and outside the pit.
Some of the common reactions that occur within the pit are presented in Eqs. 95-100 as described by Wranglen (264). These reactions include the dissolution of iron from the inner walls and bottom of the pit (Eq. 95), the hydrolysis of Fe$^{++}$ ions that generate H$^+$ ions and results in lowering the pH within the pit (Eq. 96).

\[
Fe = Fe^{++} + 2e 
\]
\[
Fe^{++} + H_2O = FeOH^+ + H^+ \quad (96 \text{ A})
\]
\[
\log \frac{FeOH^+}{Fe^{++}} = pH - 7 \quad (96 \text{ B})
\]

Other reactions that occur within the pit are the enrichment of the pit solution with aggressive anions such as Cl$^-$ (Eq. 97), and SO$_4^{2-}$ (Eq. 98) by diffusion, resulting in formation of soluble salts.

\[
Fe^{++} + 2Cl^- = FeCl_2 \quad (97)
\]
\[
Fe^{++} + SO_4^{2-} = FeSO_4 \quad (98)
\]

The reactions within the pit are aided by the production of H$_2$S from the dissolution of sulfide inclusion (Eq. 99) and the evolution of hydrogen gas (Eq. 100).

\[
MnS + 2H^+ = H_2S + Mn^{++} \quad (99 \text{ A})
\]
\[
\log H_2S = 3 - 2 \text{ pH} \quad (99 \text{ B})
\]
\[
2H^+ + 2e = H_2 \quad (100)
\]

The chemical reactions that occur at the mouth of the pit are shown in Eqs. 101-106. Three types of reactions are prevalent, including the oxidation reactions of Fe$^{++}$ ions (Eq. 101) and FeOH$^+$.
Neutral, Aerated NaCl solution → O₂ porous crust

O₂ + 2H₂O + 4e⁻ = 4OH⁻

Mill scale

Fe₃O₄ → FeOOH

Red rust FeOOH

Black rust Fe₃O₄

Steel

MnS + 2H⁺ = H₂S + Mn⁺

Concentrated Acid Pit Solution FeCl₂, HCL, H₂S

Occasional precipitation of solid salt

Fig. 41. Autocatalytic Nature of Pitting Corrosion of Steel in Neutral Aerated Solution Containing Chloride Ions (264).

(Eq. 102) by dissolved oxygen; the hydrolysis reactions of Fe⁺⁺⁺ (Eq. 103) and FeOH⁺⁺ ions (Eq. 104) and the precipitation reactions of magnetite or black rust (Eq. 105) and red rust (Eq. 106) as suggested by Wranglen (264).

\[
2\text{Fe}^{+++} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ = 2\text{Fe}^{++++} + \text{H}_2\text{O} \quad (101)
\]

\[
2\text{FeOH}^{++} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ = 2\text{FeOH}^{+++} + \text{H}_2\text{O} \quad (102)
\]

Hydrolysis Reactions:

\[
\text{Fe}^{+++} + \text{H}_2\text{O} = \text{FeOH}^{+++} + \text{H}^+ \quad (103 \text{ A})
\]

\[
\log \frac{\text{FeOH}}{\text{Fe}^{+++}} = \text{pH} - 2.5 \quad (103 \text{ B})
\]
\[ \text{Precipitation reactions:} \]

\[ \begin{align*}
\text{FeOH}^{2+} + H_2O &= \text{Fe(OH)}_2^+ + H^+ \\
\log \frac{\text{Fe(OH)}_2^+}{\text{FeOH}^{2+}} &= \text{pH} - 3.5
\end{align*} \] (104 A)

Finally, the reduction of dissolved oxygen (Eq. 107) and rust (Eq. 108) both take place outside the pit.

\[ \begin{align*}
0_2 + 2H_2O + 4e &= 4OH^- \\
3\text{FeOOH} + e &= \text{Fe}_3\text{O}_4 + H_2O + OH^- 
\end{align*} \] (107)

These reactions indicate that the conditions inside and outside of the pit differ in many aspects. For example, reducing conditions such as the presence of low dissolved oxygen, high acidity or low pH, high concentrations of aggressive ions and high electrical conductivity prevail inside the pit, all of which promote the dissolution of the metal (264). The conditions outside the pit are generally oxidizing, with high dissolved oxygen content and are slightly alkaline which favors passivation. The oxidizing and reducing conditions are further aided by the growth of hydrated tubercles deposited at the mouth of the pit that hinder the free mixing of the pit solution with the bulk electrolyte.
Statistical Evaluation

Since corrosion of metals is affected by many factors, extreme caution should be exercised in reporting and interpreting those results that are based on a limited number of tests. To verify if the rates of corrosion, as affected by different variables, were statistically different from each other, a number of tests were replicated twelve times using Water A (Table 8). The average, the minimum and the maximum rates of corrosion of mild steel as determined by both weight loss and Corrator probes are shown in Tables 13 and 14 respectively.

Table 13. The Average, Minimum and Maximum Rates of Corrosion of Mild Steel by Weight Loss, pH 8.00

<table>
<thead>
<tr>
<th>Set No.</th>
<th>Chlorine (mg/l)</th>
<th>Color* (pcu)</th>
<th>4 days</th>
<th>11 days</th>
<th>18 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>0</td>
<td>12.2</td>
<td>8.0</td>
<td>17.0</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>15</td>
<td>16.4</td>
<td>9.0</td>
<td>26.0</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>0</td>
<td>14.7</td>
<td>11.0</td>
<td>21.0</td>
</tr>
<tr>
<td>4</td>
<td>0.0</td>
<td>15</td>
<td>12.0</td>
<td>10.0</td>
<td>15.0</td>
</tr>
</tbody>
</table>

* Standard Platinum Cobalt units, tests run with 12 replicates.

The averages are plotted in Figs. 42 and 43 as determined by the weight loss and Corrator methods respectively. The following statistics were calculated for the 18-day exposure tests for both Corrator and weight loss data. The average rates of corrosion, \( \bar{X} \) were calculated to determine the central tendency of the data (Eq. 109).
Fig. 42. Average Rate of Corrosion of Mild Steel by Weight Loss, pH = 8.00.

- No Chlorine or color
- 1.00 mg/l chlorine and 15 pcu color
- 15 pcu color
- 1.00 mg/l chlorine

Fig. 43. Average Rate of Corrosion of Mild Steel by Corrator Probes, pH 8.00.

- No Chlorine or color
- 1.00 mg/l chlorine and 15 pcu color
- 15 pcu color
- 1.00 mg/l chlorine
The minimum and maximum rates of corrosion were included in Tables 13 and 14 to indicate the dispersion or spread of the data. In addition, the standard deviation, S, and the 95% confidence interval CI were also calculated for the data. The following computations were necessary for the calculation of the standard deviation and the 95% confidence interval (266).

## Table 14. Average, Minimum and Maximum Rates of Corrosion of Mild Steel by Corrator Probes, pH 8.00

<table>
<thead>
<tr>
<th>Set No.</th>
<th>Chlorine/Color (mg/l)</th>
<th>Corrosion Rate, mpy</th>
<th>4 days</th>
<th>11 days</th>
<th>18 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0/0</td>
<td>10.1</td>
<td>5.9</td>
<td>10.4</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.0/15</td>
<td>12.5</td>
<td>1.6</td>
<td>17.4</td>
<td>14.8</td>
</tr>
<tr>
<td>3</td>
<td>1.0/0</td>
<td>10.6</td>
<td>0.8</td>
<td>14.9</td>
<td>12.4</td>
</tr>
<tr>
<td>4</td>
<td>0.0/15</td>
<td>8.5</td>
<td>4.0</td>
<td>12.1</td>
<td>9.1</td>
</tr>
</tbody>
</table>

\[
\text{Average} = \bar{X} = \frac{\sum X_i}{n} = \frac{X_1 + X_2 + X_3 \ldots + X_n}{n} = \frac{i=1}{n} \tag{109}
\]

\[
\sum X_i^2 - (\sum X_i)^2 / n = SS
\]

\[
S^2 = \frac{\sum X_i^2 - (\sum X_i)^2}{n-1} = \frac{SS}{df} \tag{110}
\]
where $S^2$ is the sample variance of mean square, $SS$ is the sum of squares, $df$ is the degrees of freedom and $n$ is the number of observations.

\[
\text{standard deviation} = s = \sqrt{\frac{S^2}{n}} \tag{111}
\]

\[
\text{standard error of a mean} = S = \frac{S}{\sqrt{n}} \tag{112}
\]

\[
95\% \text{ CI} = \bar{X} \pm t_{0.05} \frac{S}{\sqrt{n}} \tag{113}
\]

The average values of the corrosion rate data of Tables 13 and 14 for the 18-days exposure period were compared to each other using both analysis of variance (ANOVA) and the student $t$-test. Similar calculations were carried out for the Corrator data of Table 14. In order to find out if the rates of corrosion as determined by weight loss and Corrator methods were statistically different, the corresponding average values were also compared.

The following statistics were employed in comparison of the means of the two sets of tests, using the $t$ test (Eqs. 114-119).

\[
t = \frac{\bar{x}_1 - \bar{x}_2}{\frac{S^2}{n_1 - n_2} + \frac{S^2}{n_2}} = \frac{\bar{d}}{S_d} \tag{114}
\]

\[
S^2_w = \frac{s^2_1 + s^2_2}{2} \tag{115}
\]
where $S_w$ is the weighted average of the sample variances, for an equal number of observations.

$$S_d = \sqrt{\frac{2S_w^2}{n}}$$  \hspace{1cm} (116)

$$df = 2(n-1)$$  \hspace{1cm} (117)

$$95\% CI = \bar{d} \pm t_{0.05} S_d$$  \hspace{1cm} (118)

If $|t| > t_{0.05}$, the difference is said to be significant, and if $|t| > t_{0.01}$, the difference is said to be highly significant.

The F test which utilizes analysis of variance, ANOVA, requires the following numerical calculations for the comparisons of two or more means. If $r$ is the number of replicates, in this case 12, and $t$ is the number of treatments or alternatives to be compared, then,

$$C = \frac{\sum X_i^2}{rt} = \frac{\left(\sum X_{ij}\right)^2}{rt}$$  \hspace{1cm} (119)
where $C$ is a correction term, and $S_{ij}$ is the $j$th observation on the $i$th treatment, $i = 1, 2 \ldots t$, and $j = 1, 2 \ldots r$.

Total $SS = \sum_{ij} X_{ij}^2 - C \quad (120)$

$$\sum_{i=1}^{t} \frac{\sum_{i=1}^{t} (X_{i.})^2}{r} - C \quad (121)$$

Treatment $SS = \frac{\sum_{i=1}^{t} (X_{i.})^2}{r} - C \quad (121)$

Error $SS = Total SS - Treatment SS \quad (122)$

The mean square values $S^2$ for the treatment and the error are calculated by dividing the treatment and the error $SS$ to their corresponding degrees of freedom. The $F$ statistic is calculated by dividing the treatment mean square by the error mean square. If the calculated $F$ value is greater than the tabulated $F$ value at a given level of significance, the two tests are said to be significantly different at that level. When comparing the means of two samples, the square root of $F$ has student's $t$ test distribution (266).

Some of the statistical results are presented in Table 15. Both the analysis of variance and the $t$ statistic revealed a highly significant difference among some of the four sets of tests when a comparison of their means was made.
Table 15. Statistical Results of the Corrosion Rates of Mild Steel, 18-day Exposure

<table>
<thead>
<tr>
<th>No.</th>
<th>Cl₂/Color*</th>
<th>Corrosion Rate, mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\bar{x}$</td>
</tr>
<tr>
<td>1</td>
<td>0.0</td>
<td>11.6</td>
</tr>
<tr>
<td>2</td>
<td>1.0/15</td>
<td>21.8</td>
</tr>
<tr>
<td>3</td>
<td>1.0/0</td>
<td>21.7</td>
</tr>
<tr>
<td>4</td>
<td>0/15</td>
<td>9.7</td>
</tr>
</tbody>
</table>

* Chlorine in mg/l and color in pcu's.

In the weight loss data, no difference in corrosion rate was detected at the 95% level of confidence between sets 1 and 4, and sets 2 and 3. This means that natural color did not influence the rates of corrosion. The difference in rates of corrosion was found to be highly significant (99% level of confidence) between sets 1 and 2; sets 1 and 3; sets 2 and 4 and sets 3 and 4, meaning that chlorine accelerated the rate of corrosion of steel.

In comparison of the Corrator data, a highly significant difference (0.99 confidence level) was observed between sets 1 and 2; and sets 2 and 4. A significant difference (0.95 confidence level) was seen between sets 1 and 3, and sets 3 and 4. No difference was detected between sets 1 and 4 and sets 2 and 3.

When the rates of corrosion obtained by the weight loss were compared with those measured by the Corrator, on a one-to-one basis, no statistically significant difference was detected except in sets 3
which were different at 95% level of confidence. Although the results of the Corrator measurements were numerically lower than the rates measured by weight loss, the statistical analysis of the data indicates a satisfactory correlation between these two measurement techniques.

Corrosion of Copper

According to Cohen and Lyman (215), over 6 million miles (7 billion pounds) of copper tube have been used for plumbing in the United States since World War II. This increased use of copper is attributed to its satisfactory performance under normal conditions of exposure. However, copper like any other material of construction is not immune to corrosion. Certain operating conditions and water quality parameters have been found to cause premature failure of copper pipes.

Several experiments were conducted on copper under laboratory conditions to evaluate its rate of corrosion in synthetic solutions of different qualities. The test conditions closely matched those of the mild steel experiments, except that longer exposure time was necessary for copper because of lower corrosion rates. A number of tests were also performed under laboratory conditions on an actual supply water from Pinellas County, Florida that had been shown to be corrosive to copper services. The actual water used in the tests had the following chemical composition: pH = 7.78; Ca$^{++}$ = 81 mg/l; Mg$^{++}$ = 8 mg/l; Na$^{+}$ = 14 mg/l; Cl$^{-}$ = 41 mg/l; SO$_4^{2-}$ = 17 mg/l and alkalinity = 186 mg/l, expressed as CaCO$_3$. 
Effect of Water Quality and Exposure Time

The rates of corrosion of copper in aerated waters of different chemical compositions (Table 16) are presented in Fig. 44, from which two conclusions can be drawn. First, that the rate of corrosion of copper decreased almost linearly with exposure time. Second, no real difference in rate of corrosion of copper can be noted on the basis of the water quality. The type of corrosion observed was general, with no visible pitting. Most of the copper specimens remained bright throughout the exposure period, while few specimens experienced discoloration and had a brownish appearance. A possible explanation for the absence of pitting in the copper corrosion tests may be the uniformity of the exposed surface of the copper specimens. It has been shown (267) that surface inhomogeneity (mill scale, localized carbon films or irregular oxide films) causes the pitting of copper.

Table 16. Rate of Corrosion of Copper in Aerated Solutions, by Weight Loss Method

<table>
<thead>
<tr>
<th>Type of Water*</th>
<th>Color (pcu)</th>
<th>Corrosion Rate, mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>15 days</td>
</tr>
<tr>
<td>A</td>
<td>0</td>
<td>1.91</td>
</tr>
<tr>
<td>A</td>
<td>15</td>
<td>2.13</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>1.98</td>
</tr>
<tr>
<td>B</td>
<td>15</td>
<td>2.75</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>1.78</td>
</tr>
<tr>
<td>C</td>
<td>15</td>
<td>1.95</td>
</tr>
</tbody>
</table>

* For composition of the type of water, refer to Table 8.
Fig. 44. Effect of Water Quality on the Rate of Corrosion of Copper in Aerated Solutions.
Obrecht and Quill (204-209) in a series of static and dynamic tests on the corrosion of copper concluded that the quality of water alone is not a significant factor, but that temperature, velocity, dissolved oxygen, and other operating conditions play important roles in copper dissolution. Cole (200) noted the satisfactory use of copper tubes in waters that were similar in chemical composition to those used in this study (Table 8). The rates of corrosion of copper in the tap water in both aerated and deaerated systems are shown in Figs. 45 and 46.

The rates of corrosion of copper (Tables 17-18) were found to decrease with increasing time. The rate of dissolution of copper declined at a faster rate in the tap water than in synthetic solutions. This could be attributed to the presence of high calcium and alkalinity in the natural water and the development of a protective calcite coating on the surface of the metal. The instantaneous rate of corrosion of copper (Fig. 46) shows a greater scatter in the data, although the general trend is similar to that of the weight loss data.

**Effect of pH**

The rates of corrosion of copper as determined by the weight loss methods in the tap water, was found to be independent of pH over the range 7.40-8.00. Fig. 47 is a plot of these data. No correlation was observed between pH and the instantaneous corrosion rate values.

Newel (220) reported that of the three variables, pH, temperature and velocity, the effect of pH on the rate of corrosion of
Fig. 45. Rate of Corrosion of Copper Against Time by Corrator.

- □□ Aerated, chlorine, 1.0 mg/l
- ○○ Deaerated, chlorine, 1.0 mg/l
- ●● Aerated, no chlorine
- △△ Deaerated, no chlorine
Fig. 46. Corrosion Rate of Copper Against Time by Weight Loss Method.

- □ — □ Aerated, chlorine = 1.0 mg/l
- ○ — ○ Deaerated, chlorine 1.0 mg/l
- ● — ● Aerated, no chlorine
- △ — △ Deaerated, no chlorine
Fig. 47. Corrosion Rate of Copper Against pH at Two Exposure Times. Weight Loss Method.

Aerated, chlorine = 1.0 mg/l
Deaerated, chlorine = 1.0 mg/l
Aerated, no chlorine
Deaerated, no chlorine
Table 17. Average Rate of Corrosion of Copper in mpy by Corrator Method

<table>
<thead>
<tr>
<th>pH</th>
<th>Chlorine (mg/l)</th>
<th>1 Day</th>
<th>15 Day</th>
<th>35 Day</th>
<th>55 Day</th>
<th>60 Day</th>
<th>91 Day</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A* N</td>
<td>A N</td>
<td>A N</td>
<td>A N</td>
<td>A N</td>
<td>A N</td>
</tr>
<tr>
<td>7.40</td>
<td>0.0</td>
<td>0.048</td>
<td>0.006</td>
<td>0.033</td>
<td>0.012</td>
<td>0.021</td>
<td>0.012</td>
</tr>
<tr>
<td>7.40</td>
<td>1.0</td>
<td>0.186</td>
<td>0.060</td>
<td>0.156</td>
<td>0.051</td>
<td>0.180</td>
<td>0.083</td>
</tr>
<tr>
<td>7.60</td>
<td>0.0</td>
<td>0.045</td>
<td>0.024</td>
<td>0.030</td>
<td>0.015</td>
<td>0.015</td>
<td>0.012</td>
</tr>
<tr>
<td>7.60</td>
<td>1.0</td>
<td>0.077</td>
<td>0.054</td>
<td>0.082</td>
<td>0.038</td>
<td>0.050</td>
<td>0.038</td>
</tr>
<tr>
<td>7.80</td>
<td>0.0</td>
<td>0.072</td>
<td>0.045</td>
<td>0.045</td>
<td>0.006</td>
<td>0.030</td>
<td>0.009</td>
</tr>
<tr>
<td>7.80</td>
<td>1.0</td>
<td>0.159</td>
<td>0.064</td>
<td>0.146</td>
<td>0.078</td>
<td>0.111</td>
<td>0.088</td>
</tr>
<tr>
<td>8.00</td>
<td>0.0</td>
<td>0.045</td>
<td>0.024</td>
<td>0.030</td>
<td>0.012</td>
<td>0.018</td>
<td>0.012</td>
</tr>
<tr>
<td>8.00</td>
<td>1.0</td>
<td>0.121</td>
<td>0.082</td>
<td>0.092</td>
<td>0.036</td>
<td>0.115</td>
<td>0.068</td>
</tr>
</tbody>
</table>

* A = air saturate, N = deaerated with N₂ gas.
copper was the lowest of the three variables, and also noted that the rate of corrosion of copper (general corrosion) increased with decreasing pH in the pH range 3-6.5. However, the pH of most drinking waters lies between pH 6.5 - 8.5.

<table>
<thead>
<tr>
<th>pH</th>
<th>Chlorine (mg/l)</th>
<th>2 Days</th>
<th>15 Days</th>
<th>91 Days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>7.40</td>
<td>0.0</td>
<td>0.93</td>
<td>0.50</td>
<td>0.26</td>
</tr>
<tr>
<td>7.40</td>
<td>1.0</td>
<td>1.32</td>
<td>1.00</td>
<td>0.50</td>
</tr>
<tr>
<td>7.60</td>
<td>0.0</td>
<td>0.98</td>
<td>0.50</td>
<td>0.25</td>
</tr>
<tr>
<td>7.60</td>
<td>1.0</td>
<td>1.17</td>
<td>1.10</td>
<td>0.60</td>
</tr>
<tr>
<td>7.80</td>
<td>0.0</td>
<td>0.90</td>
<td>0.53</td>
<td>0.26</td>
</tr>
<tr>
<td>7.80</td>
<td>1.0</td>
<td>1.42</td>
<td>0.97</td>
<td>0.74</td>
</tr>
<tr>
<td>8.00</td>
<td>0.0</td>
<td>0.95</td>
<td>0.48</td>
<td>0.25</td>
</tr>
<tr>
<td>8.00</td>
<td>1.0</td>
<td>1.41</td>
<td>1.03</td>
<td>0.50</td>
</tr>
</tbody>
</table>

* A = Air-saturated, N = deaerated with N₂ gas.

Cohen and Lyman (215), on the other hand, documented that the pitting of copper in 65 U.S. waters was prevalent in the pH range 7.00 to 7.8. Mattsson and Fredriksson (214) reported that copper failure due to pitting in hot water systems occurred in waters of low pH (< 7) and low bicarbonate alkalinity. These conflicting data suggest that the pH of the water alone may not be responsible
for pitting. Other conditions such as the overall chemistry of the water, temperature, velocity, and the type and surface conditions of copper pipe have to be considered.

**Dissolved Oxygen**

Dissolved oxygen was found to be the second most significant factor in copper corrosion after chlorine residual. Referring to Fig. 45-47, it is seen that the lowest rates of corrosion occurred in all deaerated systems containing no chlorine. The dissolved oxygen content of the aerated systems varied from 8.40–8.70 mg/l, while the concentration of dissolved oxygen in the deaerated jars ranged from 0.1–0.4 mg/l. Dissolved oxygen is an oxidizing agent that is necessary for the corrosion of copper in aqueous solutions (268). The solubility of oxygen decreases with both increasing temperature and mineral concentration of a solution.

Obrecht (268) showed in a series of short-term tests that oxygen was required for the corrosion of copper, implying that without the presence of dissolved oxygen, the corrosion of copper was unmeasurable. Obrecht (268) concluded that in a closed system, the concentration of dissolved oxygen in the solution dropped as the corrosion of copper continued. When solid copper is immersed in water containing dissolved oxygen, thermodynamically, copper will corrode forming cuprous (Cu⁺) and cupric (Cu²⁺) ions (204), because of the high redox potential of the solution. The anodic and cathodic reactions for copper corrosion are shown in reactions 123-126.
Anode: \[ \text{Cu} = \text{Cu}^+ + e \] \[ \text{Cu} = \text{Cu}^{++} + 2e \] \[ 2\text{Cu}^+ + 2\text{H}^+ + \frac{1}{2}\text{O}_2 = 2\text{Cu}^{++} + \text{H}_2\text{O} \] (123)
(124)
(125)

Cathode: \[ \text{O}_2 + 2\text{H}_2\text{O} + 4e = 4\text{OH}^- \] (126)

From these reactions, it is evident that the rate of dissolution of copper is dependent on the amount of dissolved oxygen present and the removal of dissolved copper ions either by precipitation or complexation.

**Chlorine Residual**

Of all the variables tested to determine their effects on the rate of corrosion of copper, chlorine residual proved to be the most important factor. Figs. 45-47 indicate that the corrosion attack was severe in all chlorinated systems compared to those without chlorine. The rate of corrosion was the highest in all aerated systems containing chlorine, followed by those containing chlorine but very little dissolved oxygen (0.1 - 0.4 mg/l).

Lane and Neff (190) reported that the presence of 2 mg/l free chlorine residual was responsible for the erosion-corrosion of copper in a cold water system despite a low flow velocity.

**Natural Color**

The presence of natural color at 15 pcu was found to increase the rate of corrosion of copper slightly in all synthetic solutions. The effect of color on the rate of corrosion of copper in water A (Table 8) is presented in Fig. 48. Similar effects were observed in the other waters.
Fig. 48. Effect of Natural Color on the Rate of Corrosion of Copper in Aerated Water A.

- • - • 15 Color Units
- O — O No Color
Table 19. Average Rates of Corrosion of Copper in Chloride and Sulfate Solutions, by Weight Loss Method

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Cl⁻ or SO₄²⁻ (mg/l)</th>
<th>Chemical Compound</th>
<th>Corrosion Rate, mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>15 days</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>NaCl</td>
<td>1.63</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>NaCl</td>
<td>2.12</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>NaCl</td>
<td>2.36</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>CaCl₂</td>
<td>2.18</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>CaCl₂</td>
<td>2.05</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>CaCl₂</td>
<td>2.21</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>MgCl₂</td>
<td>2.25</td>
</tr>
<tr>
<td>8</td>
<td>50</td>
<td>MgCl₂</td>
<td>1.97</td>
</tr>
<tr>
<td>9</td>
<td>100</td>
<td>MgCl₂</td>
<td>2.26</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>Na₂SO₄</td>
<td>2.13</td>
</tr>
<tr>
<td>11</td>
<td>50</td>
<td>Na₂SO₄</td>
<td>1.87</td>
</tr>
<tr>
<td>12</td>
<td>100</td>
<td>Na₂SO₄</td>
<td>2.06</td>
</tr>
<tr>
<td>13</td>
<td>10</td>
<td>CaSO₄</td>
<td>2.14</td>
</tr>
<tr>
<td>14</td>
<td>50</td>
<td>CaSO₄</td>
<td>2.08</td>
</tr>
<tr>
<td>15</td>
<td>100</td>
<td>CaSO₄</td>
<td>1.95</td>
</tr>
<tr>
<td>16</td>
<td>10</td>
<td>MgSO₄</td>
<td>1.81</td>
</tr>
<tr>
<td>17</td>
<td>50</td>
<td>MgSO₄</td>
<td>2.02</td>
</tr>
<tr>
<td>18</td>
<td>100</td>
<td>MgSO₄</td>
<td>1.16</td>
</tr>
</tbody>
</table>
The increase in rate of corrosion of copper in the presence of color could be attributed to the complexation of dissolved copper by color. Such an effect was not observed in the corrosion of mild steel. A possible explanation for this effect could be the slow rate of dissolution of copper, implying that as soon as the copper ions are released to solution, they are tied by color molecules. This reduces the concentration of dissolved copper in solution, thus favoring further dissolution of copper. Whereas in steel, the oxidation reaction is fast, and color is probably complexed at the initial states of exposure by ferrous ions.

**Effect of Specific Ions**

A series of experiments were conducted on copper specimens to evaluate the effects of chloride, sulfate and bicarbonate ions on the rate of corrosion. The chemical compounds employed in the tests included NaCl, CaCl$_2$.2H$_2$O, and MgCl$_2$.6H$_2$O for evaluating the effects of chloride ions, while salts of Na$_2$SO$_4$, CaSO$_4$ and MgSO$_4$.7H$_2$O were used for preparing SO$_4^{2-}$ solutions. In some of the tests a combination of all three compounds for each ion were used, thus the final solution contained all three cations (Na$^+$, Ca$^{++}$ and Mg$^{++}$) but only one anion, either Cl$^-$ or SO$_4^{2-}$. In other tests a combination of both chloride and sulfate ions were tested, both with and without alkalinity. Sodium bicarbonate was used as the source of alkalinity where applicable.

The average rates of corrosion of copper (Tables 19-20) as affected by concentrations of chloride and sulfate ions are presented in Figs. 49-51. The rate of corrosion of copper after 45 days of exposure was found to be higher in chloride solutions than in sulfate solutions.
(Fig. 49), as determined by the weight loss method. However, the Corrator data did not reveal any appreciable difference between the rates of corrosion of copper in Cl\(^-\) and SO\(_4\)\(^-\) solutions (Fig. 50). The rates of corrosion as determined by Corrator were significantly lower than those calculated by the weight loss method.

The effects of alkalinity on the rate of corrosion of copper (Table 21) in solutions containing both Cl\(^-\) and SO\(_4\)\(^-\) ions are presented in Fig. 52. Increasing alkalinity tended to decrease the rate of attack of copper, though the difference as indicated in Fig. 52 was minimal.

The rate of corrosion of copper as affected by the ratio of Cl\(^-\) + SO\(_4\)\(^-\) \(\text{Alkalinity} \), where the ratio is expressed in millequivalents, is presented in Fig. 53. Obrecht (268) showed that the corrosion of copper was not influenced by the presence of sodium carbonate ( <40 ppm) and sodium bicarbonate (400 ppm), while both Cl\(^-\) and SO\(_4\)\(^-\) ions were shown
Fig. 49. Effect of Chloride and Sulfate Ions on the Rate of Corrosion of Copper in Aerated Solutions, Weight Loss Method. Exposure Time 45 days.

Fig. 50. Effect of Chloride and Sulfate Ions on the Rate of Corrosion of Copper in Aerated Solutions. Corrator Method. Exposure Time 44 days.
Fig. 51. Effect of Chloride and Sulfate on the Rate of Corrosion of Copper In Solutions of Different Chemical Compounds.

- 100 mg/l Cl\(^-\), NaCl
- 100 mg/l Cl\(^-\), CaCl\(_2\)
- 100 mg/l Cl\(^-\), MgCl\(_2\)
- 100 mg/l SO\(_4^{2-}\), Na\(_2\)SO\(_4\)
- 100 mg/l SO\(_4^{2-}\), CaSO\(_4\)
- 100 mg/l SO\(_4^{2-}\), MgSO\(_4\)
to increase the rate of corrosion of copper even at low concentrations. Stumm and Champlin (267), on the other hand reported that an increase in $C_t$, the concentration of total carbonic species, decreased the rate of corrosion of copper at a given pH value. The $C_t$ values used ($10^{-1} - 10^{-2}$ M) however, were far greater than those normally encountered in potable waters.

Table 21. Average Rate of Corrosion of Copper as Affected by Alkalinity of Water in Aerated Solutions

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Concentration, mg/l</th>
<th>Corrosion Rate, mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cl$^-$/SO$_4^{2-}$/Alkalinity*</td>
<td>15 days</td>
</tr>
<tr>
<td>1</td>
<td>5/5/0</td>
<td>2.13</td>
</tr>
<tr>
<td>2</td>
<td>25/25/0</td>
<td>2.37</td>
</tr>
<tr>
<td>3</td>
<td>50/50/0</td>
<td>1.99</td>
</tr>
<tr>
<td>4</td>
<td>5/5/25</td>
<td>1.92</td>
</tr>
<tr>
<td>5</td>
<td>25/25/25</td>
<td>2.30</td>
</tr>
<tr>
<td>6</td>
<td>50/50/25</td>
<td>2.23</td>
</tr>
<tr>
<td>7</td>
<td>5/5/100</td>
<td>2.41</td>
</tr>
<tr>
<td>8</td>
<td>25/25/100</td>
<td>2.59</td>
</tr>
<tr>
<td>9</td>
<td>50/50/100</td>
<td>2.08</td>
</tr>
<tr>
<td>10</td>
<td>5/5/200</td>
<td>2.05</td>
</tr>
<tr>
<td>11</td>
<td>25/25/200</td>
<td>2.15</td>
</tr>
<tr>
<td>12</td>
<td>50/50/200</td>
<td>1.90</td>
</tr>
</tbody>
</table>

* Alkalinity is expressed in mg/l as CaCO$_3$. Corrosion rates determined by weight loss method.

Cohen and Lyman (215) in an analysis of pitting corrosion of copper reported that in 54 waters that pitted copper pipes, the concentrations of chloride were less than 75 ppm in more than 80% of the
Fig. 52. Effect of Bicarbonate Alkalinity on the Rate of Corrosion of Copper in Aerated Solutions Containing 5 mg/l of Chloride and Sulfate Ions.

- No Alkalinity
- 25 mg/l Alkalinity as CaCO₃
- 100 mg/l Alkalinity as CaCO₃
- 200 mg/l Alkalinity as CaCO₃

\[
\frac{\text{Cl}^- + \text{SO}_4^{2-}}{\text{Alkalinity}}, \text{ meq.}
\]

Fig. 53. Effect of \( \frac{\text{Cl}^- + \text{SO}_4^{2-}}{\text{Alkalinity}} \) on the Rate of Corrosion of Copper in Aerated Solutions.
waters. However, most of these waters were high in sulfate content, approximately 3 to 4 times that of chloride concentrations.

**Redox Potential**

Since corrosion of metals is an electrochemical process, and is affected by the oxidation-reduction capacity of the water, attempts were made to monitor the redox potential in selected jars. The results of redox potential measurements in Pinellas County tap water are presented in Fig. 54. Electrode potential data in synthetic waters A and B (Table 22) are shown in Fig. 55. From the data presented in Fig. 54, it is evident that redox potential values in the chlorine containing systems were in direct agreement with the measured rates of corrosion in those systems. In other words, the higher the redox potential of a solution, the greater the rate of corrosion in that particular system.

<table>
<thead>
<tr>
<th>Water</th>
<th>0 day</th>
<th>3 days</th>
<th>6 days</th>
<th>9 days</th>
<th>12 days</th>
<th>15 days</th>
<th>18 days</th>
<th>20 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>483</td>
<td>492</td>
<td>500</td>
<td>504</td>
<td>501</td>
<td>514</td>
<td>511</td>
<td>514</td>
</tr>
<tr>
<td>B</td>
<td>501</td>
<td>494</td>
<td>489</td>
<td>490</td>
<td>492</td>
<td>492</td>
<td>495</td>
<td>497</td>
</tr>
</tbody>
</table>

The measured $E_H$ values in water B were plotted on the copper $E_H - pH$ diagram (Fig. 56). All measured redox potential values coincided with the region of stability of $Cu_3(OH)_2(CO_3)_2$, implying that corrosion of copper will be stifled due to the passive films as long as the film is not damaged or removed from the copper surface.
Fig. 54. Redox Potential of Copper Against Time at pH 7.40

- □ □ Aerated, chlorine = 1.0 mg/l
- ○ ○ ○ Deaerated, chlorine = 1.0 mg/l
- • • Aerated, no chlorine
- Δ Δ Δ Deaerated, no chlorine
Variation in Water Quality

In addition to analyzing the water for leaching of copper from the coupons, other water quality parameters were also monitored periodically. Dissolved oxygen, chloride, sulfate and magnesium did not vary appreciably during the tests, while both calcium and alkalinity decreased with increasing exposure time. Sodium ion increased only in those jars to which NaOH was added for pH adjustment. The addition of NaOCl for maintaining chlorine residual in solutions also increased sodium in all chlorinated jars. The leaching of copper into
Fig. 56. Pourbaix Diagram for $1.6 \times 10^{-5}$ Cu in the Presence of 100 mg/l Alkalinity as CaCO$_3$, with Measured $E_H$ Values. ● Aerated ○ Deaerated
solution is presented in Fig. 57. The dissolution of copper appears to be greater in the initial stages of exposure and decreases with increasing time, possibly due to build up of passive films on the copper surfaces.

The Nature of Corrosion

Copper pipes in domestic waters normally corrode by pitting, erosion corrosion or impingement attack (212, 215, 216). Pitting of copper is a common form of corrosion in potable waters. Cruse and Pomeroy (217) reported that certain Southern California waters pitted copper pipes so badly that failure occurred in less than one year after being in operation. The pH of the waters that support pitting was in the range 6.6-7.5, with medium to high mineral content. In other waters copper pipes were more resistant to pitting attack, lasting more than forty years. Several factors were described as the cause of this rapid pitting. Some of the factors are related to the chemistry of the water, such as pH, redox potential and the type and amount of minerals. Others are related to the metal itself, such as its surface condition and the homogeneity of the oxide film. Many other factors depend on the operation and design of the system, including velocity of flow, temperature and the quality of workmanship (215).

Impingement attack is usually characterized by roughening of the inside surface of the copper tube, due to high flow velocity and entrained solids or gases (215). The mechanism and theory of pitting of copper in drinking waters has been investigated by Lucey (213), Mattsson (219, 221) and Mattsson and Fredriksson (214). Lucey (213)
Fig. 57. Increase in Concentration of Soluble Copper in Test Waters Due to Corrosion.

- □-□ Aerated, chlorine = 1.0 mg/l
- ○-○ Deaerated, chlorine = 1.0 mg/l
- ●-● Aerated, no chlorine
- △-△ Deaerated, no chlorine
postulated the "membrane cell theory" (213: 177) which states, "pitting arises when a pocket of cuprous chloride forms beneath a porous electrically conducting membrane (usually cuprous oxide). The anodic and cathodic processes occur on the inner and outer surfaces of the membrane. Dissolution of copper occurs by reaction of hardness salts in the water with the cathodic product above the membrane" (213: 175).

The proposed model of pitting of copper, as described by Lucey (213), is shown in Fig. 58.

Fig. 58 describes the structure of the pit, comprised of a mound, a cuprous oxide membrane and a cuprous chloride pocket. The anodic and cathodic reactions that occur on the inner and outer surfaces of the pit are shown in Eq. 127-128. The anodic reaction that takes place on the inner surface of the membrane (Eq. 127) is:

$$\text{Cu}^+ = \text{Cu}^{++} + \text{e} \quad (127)$$

While the cathodic reaction on the outer surface of the oxide membrane (Eq. 128) is:

$$\text{Cu}^{++} + \text{e} = \text{Cu}^+ \quad (128)$$

Other reactions that occur within and outside the pit are illustrated in Eq. 129-130. The anodic reaction that takes place, within the mound above the pit, as influenced by the water quality (213) is shown in Eq. 129.

$$4\text{CuCl} + \text{Ca(HCO}_3\text{)}_2 + \text{O}_2 = \text{CuCO}_3\cdot\text{Cu(OH)}_2 + \text{CaCO}_3 + 2\text{CuCl}_2 \quad (129)$$
The anodic product of reaction 129 reacts with copper within the pit to generate more cuprous ions (Eq. 130).

\[
\text{Cu} + \text{Cu}^{++} = 2\text{Cu}^{+}
\]  

(130)

The role of both chloride and oxygen in pitting of copper are evident as shown in reactions 126-130. The effect of oxygen on the oxidation of cuprous chloride to cupric chloride (Eq. 131) and the production of cuprous chloride by cupric ions (Eq. 130) are also influenced by the alkalinity of the water (213).

\[
2\text{Cu}^{+} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = 2\text{(OH)}^- + 2\text{Cu}^{++}
\]  

(131)
The hydroxyl ions that are generated due to the reduction of oxygen, react with carbonate alkalinity (Eq. 131) to form carbonate that precipitates above the pit in the crust (Eq. 132).

\[ \text{OH}^- + \text{HCO}_3^- = \text{CO}_3^{2-} \]  

(132)

The hydroxyl ions also react with cupric ions, resulting in the formation of basic copper carbonate compounds.

Mattsson (219) classified pitting of copper in fresh waters to two types, according to the temperature of the system. Type I, that occurs in cold waters, and Type II that is common in hot water installations. The main causes of pitting in Type I were described to be the presence of either a carbonaceous film, or a deposit of solid CuCl on the surface of the copper. In addition the oxide membrane theory proposed by Lucey (213) was also used to explain Type I pitting. No mechanism for Type II pitting of copper has been proposed yet. Type II pitting of copper has been shown to be influenced greatly by the pH of the solution and the sulfate content of the water. The ratio of \( \text{HCO}_3^-/\text{SO}_4^{2-} \) has also been shown to affect Type II pitting. The lower this ratio, the greater the pitting tendency of copper (219).

**Galvanized Steel**

Several tests were conducted on galvanized steel to evaluate its resistance to corrosion. Galvanized steel is an important material of construction in water supply systems, and is widely employed in household plumbing.

**Effect of Water Quality and Exposure Time**

The rates of corrosion of galvanized steel specimens in aerated waters of different chemical composition (Table 23) are illustrated in
### Table 23. Corrosion Rates of Galvanized Steel in Synthetic Solutions, A,B,C

<table>
<thead>
<tr>
<th>Water*</th>
<th>Color (pcu)</th>
<th>Chlorine (mg/l)</th>
<th>10 days</th>
<th>Corrosion Rate, mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20 days</td>
</tr>
<tr>
<td>A-O</td>
<td>0</td>
<td>0</td>
<td>2.36</td>
<td>2.23</td>
</tr>
<tr>
<td>A-O</td>
<td>0</td>
<td>1</td>
<td>3.07</td>
<td>2.91</td>
</tr>
<tr>
<td>A-O</td>
<td>10</td>
<td>1</td>
<td>2.86</td>
<td>2.68</td>
</tr>
<tr>
<td>A-N</td>
<td>0</td>
<td>0</td>
<td>1.58</td>
<td>1.72</td>
</tr>
<tr>
<td>A-N</td>
<td>0</td>
<td>1</td>
<td>0.46</td>
<td>0.33</td>
</tr>
<tr>
<td>A-N</td>
<td>10</td>
<td>1</td>
<td>0.61</td>
<td>0.67</td>
</tr>
<tr>
<td>A-N</td>
<td>10</td>
<td>1</td>
<td>0.44</td>
<td>0.37</td>
</tr>
<tr>
<td>A-N</td>
<td>10</td>
<td>0</td>
<td>0.26</td>
<td>0.21</td>
</tr>
<tr>
<td>B-O</td>
<td>0</td>
<td>0</td>
<td>1.24</td>
<td>1.11</td>
</tr>
<tr>
<td>B-O</td>
<td>0</td>
<td>1</td>
<td>2.25</td>
<td>2.08</td>
</tr>
<tr>
<td>B-O</td>
<td>10</td>
<td>1</td>
<td>1.79</td>
<td>1.58</td>
</tr>
<tr>
<td>B-O</td>
<td>10</td>
<td>0</td>
<td>0.98</td>
<td>0.77</td>
</tr>
<tr>
<td>B-N</td>
<td>0</td>
<td>0</td>
<td>0.28</td>
<td>0.31</td>
</tr>
<tr>
<td>B-N</td>
<td>0</td>
<td>1</td>
<td>0.40</td>
<td>0.43</td>
</tr>
<tr>
<td>B-N</td>
<td>10</td>
<td>1</td>
<td>0.35</td>
<td>0.40</td>
</tr>
<tr>
<td>B-N</td>
<td>10</td>
<td>0</td>
<td>0.28</td>
<td>0.18</td>
</tr>
<tr>
<td>C-O</td>
<td>0</td>
<td>0</td>
<td>0.59</td>
<td>0.55</td>
</tr>
<tr>
<td>C-O</td>
<td>0</td>
<td>1</td>
<td>1.61</td>
<td>1.35</td>
</tr>
<tr>
<td>C-O</td>
<td>10</td>
<td>1</td>
<td>1.04</td>
<td>1.23</td>
</tr>
<tr>
<td>C-O</td>
<td>10</td>
<td>0</td>
<td>0.30</td>
<td>0.35</td>
</tr>
<tr>
<td>C-N</td>
<td>0</td>
<td>0</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>C-N</td>
<td>0</td>
<td>1</td>
<td>0.45</td>
<td>0.35</td>
</tr>
<tr>
<td>C-N</td>
<td>10</td>
<td>1</td>
<td>0.40</td>
<td>0.42</td>
</tr>
<tr>
<td>C-N</td>
<td>10</td>
<td>0</td>
<td>0.10</td>
<td>0.15</td>
</tr>
</tbody>
</table>

* Letters A, B and C refer to types of Water (Table 8); letter O indicates aeration and letter N shows no aeration.
Fig. 59. Rate of Corrosion of Galvanized Steel as Affected by Water Quality.

- Water A
- Water B
- Water C
Fig. 59. The effects of both water composition and time, on the rate of corrosion of the zinc coating are shown. The rate of dissolution of the zinc was greatly affected by the water quality which is illustrated by the fact that it was the highest in Water A (low mineral content) and the lowest in Water C (high mineral content).

Galvanized steel in comparison to mild steel and copper appears to be more sensitive to the changes in the chemical composition of the waters (Fig. 59). The difference in the rates of corrosion can be attributed to the formation of basic zinc carbonate on the surface of the zinc. In hard waters, the aggressive action of water on the zinc coating is hampered due to the potential of the water to form such films on the corroding metal surface. Visual inspection of the samples revealed that the corrosion product on the zinc surface was more firmly attached to the metal in hard waters than in soft waters.

Rice (23) reported similar results; that high bicarbonate hardness resulted in better protection of the galvanized steel piping. Although galvanized steel specimens were exposed to solutions without any surface preparation (such as polishing with abrasive paper), the resulting data indicate that the rates of corrosion were generally not influenced by the original quality of the zinc coating. Only two galvanized steel specimens, out of a total of 336 that were exposed in a single set of experiments, showed some rusting of the steel at selected points after 45 days of exposure.

Effect of pH

The rates of corrosion of galvanized steel, as determined by the weight loss method in aerated solutions at different pH values are
Fig. 60. Rate of Corrosion of Galvanized Steel as Affected by pH of a Solution

- - - - - O 2 days exposure

- - - - - - 10 days exposure

presented in Fig. 60. The initial rates of corrosion of galvanized steel were higher in solutions of low pH and decreased with increasing pH. As the galvanized steel specimens continued to corrode, no marked difference was observed between the rates of corrosion as a function of pH. The significance of exposure time in corrosion testing of galvanized steel is evident from Fig. 60.

Lane and co-workers (269) conducted a series of tests in hot water galvanized piping, to evaluate the effect of silicate on corrosion of galvanized steel at different pH values. They reported that at any given dosage of silicate, the rates of corrosion decreased with increasing pH in the range 7.2-9.0.
Dissolved Oxygen

The effect of dissolved oxygen on the rate of corrosion of galvanized steel is illustrated in Fig. 61. The presence of dissolved oxygen in water is a significant factor. The rates of corrosion in Waters A and C (Table 8) are much higher in aerated solutions than in deaerated solutions.

Dissolved oxygen promotes the corrosion of galvanized steel because it takes part in electrochemical reactions. Since the dissolution of zinc is favored thermodynamically in aqueous solutions, zinc from the galvanized coating is oxidized and enters solution as positive ions. On the other hand, dissolved oxygen completes the cell reaction by acting as an electron accepter and is reduced on the metal surface.

\[
\text{Zn} = \text{Zn}^{++} + 2e \quad (133)
\]

\[
0_2 + 2H_2O + 4e = 40H^- \quad (134)
\]

The lower curves of Fig. 61 were constructed based on data for galvanized steel specimens that were exposed to solutions containing 0.1-0.4 mg/l of dissolved oxygen.

Effect of Chlorine Residual

The effect of chlorine residual on the rate of corrosion of galvanized steel in aerated solutions is shown in Fig. 62. The presence of a chlorine residual greatly increased the rate of corrosion. The rates of corrosion were higher in all chlorinated systems compared to those containing no chlorine. A similar effect was observed in
Fig. 61. Rate of Corrosion of Galvanized Steel as Affected by Dissolved Oxygen.

- **Water A, Aerated**
- **Water A, Deaerated**
- **Water C, Aerated**
- **Water C, Deaerated**
Fig. 62. Effect of Chlorine Residual on the Rate of Corrosion of Galvanized Steel in Aerated Solutions.
deaerated test solutions, i.e. the rates of corrosion of galvanized steel were higher in solutions containing chlorine, though the difference was not as pronounced as in aerated systems.

Chlorine enhances corrosion of metals both by increasing the redox potential of the solution and by its reduction to chlorine ion. Dissolved oxygen and chlorine were found to have an additive positive effect.

Natural Color

The addition of natural color to water at 10 pcu's reduced the rates of corrosion of galvanized steel in all test waters (Fig. 63). The reduction in the rates of corrosion was the highest in Water A than in either Waters B or C. Rice (230) reported that the presence of natural color inhibited the corrosion of galvanized steel when used for conveying natural or zeolite-softened water. The addition of 10 pcu's of natural color also had a negative effect on the rate of corrosion of galvanized steel in chlorinated solutions. The reductions in the rates of corrosion, however, were not as pronounced as in solutions containing no chlorine.

Effect of Specific Ions

The effects of chloride, sulfate and bicarbonate ions on the rates of corrosion of galvanized steel in aerated solutions are summarized in Fig. 64. The rates of corrosion of galvanized steel increased slightly with increasing concentrations of both chloride and sulfate ions and decreased with increasing concentrations of bicarbonate ions. Bicarbonate ions had an inhibitory effect on the rate of corrosion of galvanized steel, even in the absence of any calcium salts. The
Fig. 63. Effect of Color on the Rate of Corrosion of Galvanized Steel in Aerated Solutions.

- ○ ○ Water A, no color
- • • Water A, 10 pcu Color
- △ △ Water B, no color
- ▲ ▲ Water B, 10 pcu color
- □ □ Water C, no color
- ■ ■ Water C, 10 pcu color
Fig. 64. Effect of Chloride, Sulfate and Bicarbonate Ions on the Rate of Corrosion of Galvanized Steel in Aerated Solutions. Salts of Sodium Added. Exposure Time, 14 days.

Reduction in the rate of corrosion of galvanized steel by bicarbonate ions was probably due to the buffering effect of carbonic species in water. Sulfate ions were found to be more aggressive to galvanized
steel than were chloride ions at similar concentrations. The rates of corrosion of galvanized steel were higher in chloride and sulfate solutions, because both chloride and sulfate ions are conjugate bases of strong acids, that from soluble compounds in solutions.

The data presented in Fig. 64 were obtained from test solutions containing only one cation and one anion. The results of tests containing either chloride or sulfate ions as well as Ca$^{++}$, Mg$^{++}$ and Na$^+$ ions are illustrated in Fig. 65. The rates of corrosion, again were found to be higher in sulfate solutions than in chloride solutions. The combination of both chloride and sulfate ions in equal amounts in a single solution, gave intermediate corrosion rate values as expected. The variation of corrosion rate of galvanized steel with respect to the ratio of ($\text{Cl}^- + \text{SO}_4^{2-}$)/Alkalinity), (ratio in meq.) is shown in Fig. 66. The results indicate that the rate of corrosion increases with increasing ($\text{Cl}^- + \text{SO}_4^{2-}$)/Alkalinity) ratio.

According to U.R. Evans (270) as noted by Rice (230), the holidays and imperfections in zinc coatings are covered by the deposition of high bicarbonate hardness that protects both zinc and steel from corrosion. Hoxeng and Prutton, (226) in a study of zinc-steel couple concluded that increasing bicarbonate ions shifted the zinc potential in the anodic direction in aerated solutions. Evans (271) as noted by Hoxeng and Prutton (226) reported that chloride and sulfate ions promote the dissolution of zinc due to the high solubility of zinc chloride and zinc sulfate products at the anodic sites.
Furthermore, chloride and sulfate ions have been shown to penetrate metallic oxide films and thus initiate corrosion (226). Davies and Lotlikar (232) showed that increasing chloride concentration caused pitting of zinc in alkaline solutions, in the pH range 9.2-12.3.

**Redox Potential**

The redox potential (Table 24) of several corroding galvanized specimens were monitored periodically and the data are summarized in Fig. 67. The measured redox potential data are in close agreement.
Fig. 66. Effect of Ratio of \( \frac{\text{Cl}^- + \text{SO}_4^=}{\text{Alkalinity}} \), meq., on the Corrosion of Galvanized Steel.
with the experimentally determined corrosion rate values. This means that a positive correlation between redox potential and the rate of corrosion of galvanized steel exists. The presence of 1 mg/l of chlorine residual had a profound effect on the redox potential of both aerated and deaerated solutions. The redox potential increased slightly with increasing exposure time, in aerated systems that contained no chlorine, while it decreased slightly in all chlorinated and deaerated systems.

Table 24. Redox Potential of Galvanized Steel in Aerated Synthetic Waters.

<table>
<thead>
<tr>
<th>Water</th>
<th>Chlorine (mg/l)</th>
<th>2 days</th>
<th>8 days</th>
<th>21 days</th>
<th>30 days</th>
<th>45 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.0</td>
<td>523</td>
<td>522</td>
<td>539</td>
<td>546</td>
<td>556</td>
</tr>
<tr>
<td>B</td>
<td>0.0</td>
<td>501</td>
<td>506</td>
<td>509</td>
<td>509</td>
<td>514</td>
</tr>
<tr>
<td>C</td>
<td>0.0</td>
<td>496</td>
<td>491</td>
<td>505</td>
<td>516</td>
<td>512</td>
</tr>
<tr>
<td>A</td>
<td>1.0</td>
<td>908</td>
<td>876</td>
<td>868</td>
<td>862</td>
<td>857</td>
</tr>
<tr>
<td>B</td>
<td>1.0</td>
<td>895</td>
<td>888</td>
<td>864</td>
<td>853</td>
<td>846</td>
</tr>
<tr>
<td>C</td>
<td>1.0</td>
<td>872</td>
<td>855</td>
<td>831</td>
<td>825</td>
<td>830</td>
</tr>
</tbody>
</table>

Fig. 68 shows the redox potential measured in the study on the $E_H$ - pH diagram for zinc. Most of these redox potentials coincided with the ZnO or Zn(OH)$_2$ stability region under both aerated and deaerated conditions. Only a few redox potential measurements in aerated solutions occurred in the region of stability of Zn$^{++}$, implying active oxidation of zinc to zinc ions.
Fig. 67. Variation in Redox Potential of Galvanized Steel Immersed in Water C, pH 8.45.

- ○ ○ ○ ○ 1.0 mg/l Chlorine, Aerated
- □ □ □ □ 1.0 mg/l Chlorine, Deaerated
- ● ● ● ● No Chlorine, Aerated
- ■ ■ ■ ■ No Chlorine, Deaerated
Fig. 68. Pourbaix Diagram for $7.6 \times 10^{-5}$ M Zn in the Presence of 100 mg/l Alkalinity as CaCO$_3$, with Measured $E_H$ Values.

- Aerated
- Deaerated
Variation in Water Quality

The changes in the water quality were monitored periodically for both zinc and cadmium pick-up by solution form the exposed galvanized steel specimens (Table 25). The leaching of zinc against time is shown in Fig. 69. The concentration of zinc did not vary appreciably after two weeks of exposure time. Most of the zinc was found attached to the corroding surface of the coupons, while some zinc precipitated in the jar as corrosion continued. The concentration of soluble zinc was found to be only 10-20 percent of the total concentration of zinc. No cadmium was detected in any samples.

Table 25. Concentration of Soluble Zinc in Synthetic Solutions.

<table>
<thead>
<tr>
<th>Water</th>
<th>Dissolved Oxygen, Mg/l</th>
<th>Zinc Concentration, mg/l</th>
<th>6 days</th>
<th>15 days</th>
<th>28 days</th>
<th>45 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>8.45</td>
<td></td>
<td>1.65</td>
<td>1.82</td>
<td>2.04</td>
<td>2.22</td>
</tr>
<tr>
<td>B</td>
<td>8.43</td>
<td></td>
<td>0.84</td>
<td>0.85</td>
<td>0.85</td>
<td>0.92</td>
</tr>
<tr>
<td>C</td>
<td>8.45</td>
<td></td>
<td>0.65</td>
<td>0.71</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>A</td>
<td>0.15</td>
<td></td>
<td>0.42</td>
<td>0.45</td>
<td>0.43</td>
<td>0.58</td>
</tr>
<tr>
<td>B</td>
<td>0.20</td>
<td></td>
<td>0.28</td>
<td>0.28</td>
<td>0.29</td>
<td>0.38</td>
</tr>
<tr>
<td>C</td>
<td>0.18</td>
<td></td>
<td>0.21</td>
<td>0.20</td>
<td>0.18</td>
<td>0.27</td>
</tr>
</tbody>
</table>

The Nature of Corrosion

Corrosion of zinc is governed by many factors. The chemical composition of the solution, pH, chlorine residual, redox potential, dissolved oxygen and color, all affect the rate of corrosion of gal-
Fig. 69. Leaching of Zinc from Galvanized Steel Specimens Exposed to Different Solutions.

- Water A, Aerated
- Water A, Deaerated
- Water C, Aerated
- Water C, Deaerated
vanized steel. Zinc has been shown to passivate in dilute sodium hydroxide solutions (236) forming a thin (three monolayers) film composed of \( \text{Zn(OH)}_2 \) or \( \text{ZnO} \). The chemical reactions that lead to the passivation of zinc include:

\[
\begin{align*}
\text{Zn} & = \text{Zn}^{++} + 2e \quad (133) \\
\text{Zn}^{++} + 2\text{OH}^- & = \text{Zn(OH)}_2 \quad (135) \\
\text{Zn(OH)}_2 & = \text{ZnO} + \text{H}_2\text{O} \quad (136)
\end{align*}
\]

When bicarbonate, chloride and sulfate ions are present in a solution, the following chemical reactions take place in corrosion of zinc:

\[
\begin{align*}
\text{Zn}^{++} + \text{HCO}_3^- & = \text{ZnCO}_3 + \text{H}^+ \quad (137) \\
\text{ZnCO}_3 + \text{H}_2\text{O} & = \text{ZnO} + \text{HCO}_3^- + \text{H}^+ \quad (138) \\
\text{Zn} + \text{HCO}_3^- & = \text{ZnCO}_3 + \text{H}^+ + 2e \quad (139) \\
\text{Zn}^{++} + 2\text{Cl}^- & = \text{ZnCl} \quad (140) \\
\text{Zn}^{++} + \text{SO}_4^- & = \text{ZnSO}_4 \quad (141)
\end{align*}
\]

Zinc, as compared to iron and copper, has a simple chemistry. The rates of corrosion of zinc were strongly affected by oxygen, chlorine residual, color and alkalinity.
CHAPTER FIVE
SUMMARY AND CONCLUSIONS

Corrosion of metals in potable waters is believed to be a major cause of water deterioration in the distribution systems and is considered as a main source of adding undesirable contaminants to the finished water. The concern over the safety and health implications of the water we drink is evident from the passage of the Safe Drinking Water Act, PL 93-523 by the Congress in 1974. The law requires that the water quality regulations be met at the consumer's tap. Results of national surveys of drinking water systems indicate that 50 to 70 percent of water utilities are distributing corrosive waters to their customers in the United States (1).

The impact of corrosion on consumers is classified into three main categories: health, economic and aesthetic. The health impact of corrosion is primarily due to the addition of lead and cadmium (both cumulative poisons) to the treated water, by the corrosive action of water on pipes and plumbing fixtures. The economic significance of corrosion is due to the cost of replacement and maintenance as well as the cost of excess energy required for the operation of the plants. The cost of replacement for U.S. community water supply distribution systems has been estimated to be as high as 125 billion dollars (73). The protection of this investment is of great interest

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to the water supply industry. The aesthetic effect of corrosion is due to leaching of iron, zinc and copper from the corroding pipes into the water. Their presence in water in excess of the maximum contaminant levels (MCL) causes discoloration of water, staining of laundry and fixtures and objectionable taste and odor.

The materials most commonly used for conveying potable waters include mild steel, cast iron, copper and galvanized steel.

Although several corrosion indices have been developed in the past to predict the aggressivity of a given water, each one has serious limitations and is only applicable to specific cases. No general rule exists for identifying and measuring corrosion in domestic waters.

This study was designed to investigate the effect of various water quality parameters on the rates of corrosion of several important metals such as mild steel (low carbon steel, carbon content less than 0.3 percent), galvanized steel and copper under controlled laboratory conditions. More specifically, the effects of major cations (Ca$^{++}$, Mg$^{++}$, Na$^{+}$) and major anions such as Cl$^{-}$, SO$_4^{2-}$ and HCO$_3^-$ as well as the effects of pH, dissolved oxygen, chlorine residual and natural color on the rates of corrosion of mild steel, copper and galvanized steel were evaluated. Most of the tests were conducted in freshly prepared synthetic solutions, while some tests were performed on actual tap waters.

The existing literature on corrosion of metals in potable waters was critically reviewed. The fundamentals of corrosion, polarization and passivity as well as the electrochemical reactions necessary for
corrosion were thoroughly discussed. The chemical composition of natural waters with respect to the presence of major ions was presented. Pourbaix diagrams, which illustrate the thermodynamic behavior of metals in aqueous solutions, were constructed for the metals of our concern (Fe, Cu and Zn). The types and forms of corrosion, the factors and causes of corrosion as well as the methods of mitigation of corrosion were briefly described. The measurement of corrosion rates and the limitations of laboratory testing were pointed out. The experimental procedures such as the design of testing apparatus, the preparation of corrosion coupons and electrodes, as well as monitoring the water quality parameters and their analysis, have been treated in detail in the manuscript. The mechanisms and nature of corrosion were noted for each metal.

Corrosion rates were determined using the conventional weight loss method and the polarization resistance technique. The following conclusions can be drawn from this research.

**Mild Steel**

1. The presence of dissolved oxygen in water was found to be the main factor in corrosion of steel under all conditions that were investigated. The rates of corrosion in deaerated systems were found to be extremely low.

2. The presence of 1.5 mg/l of free chlorine residual increased the rate of corrosion in both aerated and deaerated systems.

3. Chlorine residual required frequent monitoring and adjustments. Chlorine, as a strong oxidizing agent reduces to chloride which promotes the oxidation of the metal.
4. Overall, long-term corrosion rates were higher in softer waters than in harder waters.

5. The corrosion rates were significantly affected by the exposure time, especially when the rates were determined by the weight loss method.

6. The corrosion rates were generally high because the metal specimens were polished to remove the mill scale for reproducibility of the results.

7. Short-term (3 weeks exposure time) experiments had better reproducibility than long-term (6 months) experiments.

8. The rate of corrosion was slightly higher at pH 6.00 than at pH values of 7.00 to 9.50.

9. The presence of natural color decreased the rate of corrosion of mild steel. However, the reduction was statistically insignificant.

10. The rate of corrosion of steel was not influenced by the ratio of A/V, the total area of steel specimens to the volume of solution.

11. The pH changed during the experiments but was monitored frequently and adjusted to its initial values.

12. The concentrations of both calcium and alkalinity decreased significantly during the study. The decrease was greater in hard waters. The concentrations of sodium, magnesium, chloride and sulfate in solutions remained relatively constant during the experiments.

13. The iron concentration in the solution was greatly affected by time. The maximum concentrations of Fe in aerated solutions
occurred after 24 hours of exposure. The iron pick-up gradually declined as the tests continued and iron oxides precipitated.

14. The iron pick-up was minimal in the anaerobic system.

15. In aerated systems, several layers of corrosion products were formed on the metal surface. A black layer of precipitate existed adjacent to the surface. This layer was covered with a thick layer of yellowish, gelatinous hydrated ferric oxide.

16. In deaerated systems, a uniform, thin, black passive film was formed on the exposed steel specimens, most probably magnetite, $\text{Fe}_3\text{O}_4$.

17. The response of the redox measuring electrode was slow in all test solutions. Several hours of equilibrium time was needed to establish a steady $E_H$ reading.

18. The redox potential values dropped rapidly initially, showing the onset of corrosion and the establishment of equilibrium. The $E_H$ values then gradually increased with increasing exposure time, indicating that passivation of the metal was taking place.

19. The $E_H$ values in aerated systems were higher than in deaerated systems.

20. The rates of corrosion increased with increased concentrations of both chloride and sulfate ions in aerated test solutions. However, sulfate ions tended to have higher rates of corrosion than chloride ions at similar concentrations.

21. The rates of corrosion of mild steel were generally independent of the type of cation used for preparing chloride and sulfate solutions, at the presence of carbonate alkalinity. In the absence
of carbonate alkalinity, the rates of corrosion of mild steel increased with increased concentrations of Na\(^+\) and Mg\(^{++}\) ions in solution.

22. The rates of corrosion of mild steel were higher in un-buffered solutions compared to those buffered with sodium borate.

23. The corrosion rates of mild steel as determined by the conventional weight loss method and Corrator probes were generally in good agreement. No statistically significant difference was obtained.

24. Bicarbonate alkalinity reduced the rates of corrosion of mild steel in water containing other cations and anions. The reverse was true when other ions were absent.

25. The rate of corrosion of mild steel increased with increasing ratio of \(\frac{Cl^- + SO_4^{2-}}{Alkalinity}\) beyond a ratio of 0.2.

26. Corrosion of the mild steel was of the general type, covering the entire surface of the metal.

Copper

1. The rate of corrosion of copper (by weight loss) decreased almost linearly with exposure time.

2. The rates of corrosion of copper were more reliably determined by the conventional weight loss method than by instantaneous Corrator method.

3. The rates of corrosion of copper in synthetic waters A, B and C were not different from each other.

4. The rate of corrosion was found to be independent of pH over the range 7.40-8.00 in the weight loss data. No correlation between pH and the instantaneous rate of corrosion was observed.
5. The rate of corrosion was increased by the presence of 1.0 mg/l of chlorine residual in both aerobic and anaerobic systems. Chlorine was found to be the most important factor in copper corrosion.

6. The type of corrosion was "general", with no visible pitting. Most of the copper specimens remained bright throughout the exposure period, while only a few specimens experienced discoloration and had a brownish appearance.

7. Instantaneous rate of corrosion of copper showed a greater scatter in the data compared to weight loss measurements.

8. Dissolved oxygen was found to be the second most significant factor in copper corrosion after chlorine residual. The rates of corrosion were the lowest in all deaerated systems containing no chlorine.

9. The presence of natural color at 15 pcu's was found to increase the rate of corrosion of copper slightly in all synthetic solutions.

10. The rates of corrosion of copper were higher in chloride solutions than in sulfate concentrations.

11. A significant difference was observed between the two methods of measuring of corrosion rates of copper in all chloride and sulfate solutions. The instantaneous rates of corrosion were lower than those determined by weight loss.

12. Increasing alkalinity tended to decrease the rate of attack of copper in chloride and sulfate solutions.

13. Redox potential measurements correlated well with the corrosion rates. The measured values of redox potentials coincided with
the region of stability of \( \text{Cu}_3(\text{OH}_2)(\text{CO}_3)_2 \), implying that corrosion of copper will be stifled due to passive films as long as those films are not damaged or removed from the copper surface.

14. Calcium and alkalinity of water decreased during the experiments, while other water quality parameters remained relatively constant.

15. The leaching of soluble copper to solution due to corrosive action of water was faster in the initial stages of exposure and decreased with increasing time.

16. The rate of corrosion of copper increased initially with increasing ratio of \( \frac{\text{Cl}^- + \text{SO}_4^2-}{\text{Alkalinity}} \) up to a ratio of 1.0. No increase in rate was observed beyond that ratio.

17. The values of redox potential increased slightly in solutions indicating the passivity of copper specimens.

**Galvanized Steel**

1. The rates of corrosion of galvanized steel were highly affected by the water quality. The rates of corrosion were the highest in soft, unbuffered waters.

2. The rates of corrosion of galvanized steel were influenced by the pH of the solutions. The rates of corrosion of galvanized steel were higher below pH 7.40 and above pH 8.20.

3. Chlorine residual increased the rates of corrosion of galvanized steel in both aerated and deaerated solutions, although the rates were much higher in aerated solutions.

4. Dissolved oxygen had a profound effect on the rate of corrosion of galvanized steel.
5. The presence of 10-15 pcu of color decreased the rate of corrosion of galvanized steel in test waters including chlorinated systems.

6. The rate of corrosion of galvanized steel increased slightly with increasing concentrations of both chloride and sulfate ions.

7. The rates of corrosion decreased with increasing bicarbonate concentrations in solutions.

8. Sulfate ions appeared to be more aggressive to galvanized steel than chloride ions.

9. The rates of corrosion of galvanized steel increased with $\frac{\text{Cl}^- + \text{SO}_4^{2-}}{\text{Alkalinity}}$ ratio.

10. Redox potentials of solutions and the rates of corrosion of galvanized steel were positively correlated.

11. Redox potential values increased slightly with increasing exposure time in aerated systems, while it decreased in all chlorinated and deaerated systems.

12. Most of the measured redox potential values of galvanized steel systems coincided with the region of stability of ZnO or Zn(OH)$_2$. Only a few $E_H$ values in aerated solutions occurred in the regions of stability of Zn$^{++}$, implying active oxidation of Zn to Zn$^{++}$ ions.

13. The concentrations of soluble zinc in solutions did not vary appreciably after two weeks of exposure time.

14. No cadmium leaching from the dissolved zinc coating was detected in any test.
REFERENCES


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45. Willoughby, R.A.; McDonald, E.; McSherry, B.J.; & Brown, G. The Interaction of Toxic Amounts of Lead and Zinc to Young Growing Horses. The Veterinary Record. 91:10:382 (October 14, 1972).


144. Pourbaix, M. Theses, Delft and Brussels, 1945 as quoted in Reference 140.


238. Magna Corrator Model 1120, Magna Instruments, a Division of Rohrback Corporation, 1186 East Telegraph Road, Santa Fe Springs, California 90670.


246. LaMotte-Palin Chlorine Demand Outfit, Model LP–CD (Code 6972). LaMotte Chemical Products Co., Chestertown, Maryland 21620.


BIOGRAPHICAL SKETCH

Abdul Baqi Ahmadi was born in a small rural village (Rustum-Khil) on January 22, 1945, in Logar Valley, in Afghanistan. He attended Baraki-Rajan Elementary School and Ibnī Sīna Junior High School before admission to the Afghan Institute of Technology. Upon graduation from the Afghan Institute of Technology with high honors, he attended Kabul University and obtained his B.S. in civil engineering, also with high honors, in 1968.

After serving one year in military training, he joined the College of Engineering at Kabul University as a faculty member. He was awarded a scholarship in the U.S. in September of 1970. He earned his Master of Science degree in environmental engineering from the University of Cincinnati in September 1972. Upon completion of his M.S. training, he returned to Afghanistan to pursue teaching at Kabul University. In 1975, he was granted a scholarship for advanced training in the U.S. As a result, he entered the Ph.D. program in the Department of Environmental Engineering Sciences at the University of Florida.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

John Edward Singley, Chairman
Professor of Environmental Engineering Sciences

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