PN-AAV-323

CORROSION MANUAL

PART 1

WET-PROCESS PHOSPHORIC ACID

CORROSION TESTING AND CONTROL

IN

FERTILIZER INTERMEDIATES AND PRODUCTS

INTERNATIONAL FERTILIZER DEVELOPMENT CENTER

June 1981

TABLE OF CONTENTS

Page

Acronyms and Abbreviations iii

Measures iv

Acknowledgment v

Preface vi

Introduction 1

Corrosion Fundamentals 2
- The Electrochemical Nature of Corrosion 2
- Potential, Current, and Resistivity 4
- Polarization, Passivity, and Passivation 7

Types of Corrosion 10
- Galvanic Corrosion 11
- Crevice Corrosion 13
- Pitting Corrosion 13
- Intergranular Corrosion 14
- Erosion Corrosion 15
- Stress Corrosion Cracking 15

Corrosion Protection and Control 17
- Materials Selection 17
- Coatings and Linings 18
- Cathodic and Anodic Protection 19
- Inhibitors 21

Corrosion Testing 23
- Simulation of Industrial Conditions 24
  - Concentration of Major Constituents 24
  - Effects of Impurities 24
  - Influence of pH 25
  - Influence of Temperature 25
  - Effects of Velocity 26
  - Effect of Aeration 26
- Types of Corrosion Testing 27
  - Laboratory Tests 27
  - Pilot-Plant Tests 27
  - Industrial Plant Tests 27
  - Field Tests 27

Weight-Loss Techniques 29
- Specimen Preparation 29
- Exposure Equipment and Conditions 31
- Evaluation of Results 32

TABLE OF CONTENTS (Continued)

Page

Electrochemical Techniques 34
- Potential Measurements 35
- Current-Potential Relationship 36
- Measurement of Corrosion Factors 42
  - pH Measurement 42
  - Dissolved Oxygen Measurement 42
  - Electrolytic Conductivity Measurement 43
- Corrosion Measuring Instruments 44
  - Electrical Resistance Method 44
  - Linear Polarization Resistance Instruments 44
  - The Petrolite Corrosion Rate Meter 45
  - The Potentiostats 45
  - The Potentiodyne Analyzer 45

Corrosion in Wet-Process Phosphoric Acid (WPA) 48
- Influence of Impurities 51
  - Effect of Chloride Ion 52
  - Effect of Fluoride Ion 52
  - Effect of H_2SO_4 53
  - Influence of H_2S 54
  - Influence of Oxidizers 54
- Effect of Operating Conditions 55
  - Effect of Acid Concentration 55
  - Effect of Temperature 57
  - Effect of Agitation 58
  - Effect of Organic Matter 58
- Corrosion Testing in WPA 59
  - Laboratory Tests 59
  - The Bench-Scale Wet-Process Acid Unit (BSWPA) 60
  - WPA Pilot Plant 65
- Corrosion Control in WPA Industry 69

Bibliography 73

Appendices

ACRONYMS AND ABBREVIATIONS

Organizations

AISI . . . . . American Iron and Steel Institute
API. . . . . .American Petroleum Institute
ASM. . . . . American Society of Metals
ASTM. . . . . .American Society for Testing and Materials
BSI. . . . . British Standards Institute
IFDC . . . . . International Fertilizer Development Center
ISO. . . . . International Standards Organization
NACE. . . . . National Association of Corrosion Engineers
NBS . . . . . .National Bureau of Standards
SIS. . . . . Swedish Institute of Standards
SSPC. . . . . .Steel Structures Paint Council
TVA. . . . . Tennessee Valley Authority

Other Abbreviations

BSWPA . . . . . .bench-scale wet-process acid
FGR. . . . . fiberglass epoxy or polyester
PPWPA . . . . . wet-process acid pilot plant
SCC . . . . . stress corrosion cracking
SCE . . . . . .standard calomel electrode
SHE . . . . . .standard hydrogen electrode
WPA. . . . . .wet-process acid

MEASURES

Å	Angstrom
ac	alternating current
dm^2	square decimeter
ft/sec	feet per second
g/cm^3	grams per cubic centimeter
in	inch
m/sec	meter per second
mA/cm^2	milliampere per square centimeter
mA/ft^2	milliampere per square foot
mdd or $mg/(dm^2)(day)$	milligrams per square decimeter per day
mg	milligram
mm	millimeter
mmpy	millimeter per year
mpy	mils per year
μA	microampere
$\mu A/cm^2$	microampere per square centimeter
μg	microgram
μM	micrometer
mV	millivolt
pm/sec	picometer per second
ppm	parts per million
V/amp	volt per ampere

ACKNOWLEDGMENT

The author expresses appreciation to the management of IFDC and the Fertilizer Technology Division for the opportunity to work in this organization and for the support to prepare this manual.

The encouragement and the collaboration offered by the Fertilizer Technology Division management and staff, in particular by the wet-process phosphoric acid (WPA) group, and their helpful discussions and comments on corrosion in WPA and on common testing procedures are duly acknowledged.

The author wishes to acknowledge the many items of information collected from a large body of sources that helped to enrich his professional thinking and experience and that were useful during the preparation of this manual.

The efficient and courteous assistance of the IFDC secretarial staff in expediting this manual is sincerely acknowledged.

PREFACE

The aim of this manual is to present in a concise and practical form accepted methods, techniques, standards, and procedures for the determination of the corrosion characteristics of fertilizer materials including raw materials, intermediates, and finished fertilizers.

This manual is concerned mainly with corrosion in wet-process phosphoric acid (WPA). WPA is perhaps the most important intermediate in the fertilizer industry since it is a major constituent of such fertilizers as triple superphosphate, ammonium phosphate, and mixed fertilizers.

An attempt has been made to strike a proper balance between the theoretical and practical aspects of corrosion science and engineering through use of chemical and electrochemical principles but without losing contact with laboratory and industrial plant experiences and activities. The manual may serve as a basis for training scientific and technical personnel to use the techniques discussed and for setting up a corrosion laboratory to serve the fertilizer industry in developing countries.

The procedures presented in this manual should be considered general guidelines rather than rigid instructions to be followed strictly. The procedure actually adopted will be determined by the problem at hand and limited only by the ingenuity of the investigator who uses it.

The procedures described are those now being applied in the Fertilizer Technology Division of IFDC and are based on the present facilities and instruments of the division, but other methods, techniques, and procedures for study of corrosion in fertilizer systems may be used as well.

This manual is composed of seven major sections: (1) Corrosion Fundamentals, (2) Types of Corrosion, (3) Corrosion Protection and Control, (4) Corrosion Testing, (5) Weight-Loss Techniques, (6) Electrochemical Techniques and (7) Corrosion in Wet-Process Phosphoric Acid (WPA).

Several appendices (A to N) are included in this manual to illustrate methods of corrosion testing and to present information on related areas.

In the course of further development, the manual may be expanded to include additional corrosion testing methods and techniques (see Appendix A), or it may be the first brochure of a series of future publications on the corrosion characteristics of fertilizer intermediates and products. Sources of information on corrosion control and corrosion testing are given in Appendix B.

Muscle Shoals, Alabama

M. Schorr

INTRODUCTION

The chemical nature and composition of a fertilizer determine its corrosion characteristics. Fertilizers may be acidic, neutral, or basic; their pH and hygroscopicity affect their corrosiveness in the presence of moisture. A list of fertilizer intermediates and products that illustrates their great chemical diversity is presented as Appendix C.

Corrosion problems occur in the fertilizer industry in three general areas: production, storage and transportation, and field application.

Production of fertilizers involves use of strong mineral acids: sulfuric, phosphoric, nitric, and hydrochloric; strong bases: soda ash, caustic soda, and ammonia; and salts of potassium and ammonia. All these chemicals are highly corrosive to steels and, under certain conditions, even to stainless steels; so that special stainless steels and high-cost nickel alloys may be required to avoid shutdowns resulting from corrosion problems. In the manufacture and handling of nitrogen fertilizer solutions, chromium-nickel stainless steels and aluminum alloys are satisfactorily resistant, but copper alloys and zinc are severely corroded. Corrosion in fertilizer plants may lead to contamination of products; loss of materials, equipment, and operating time; increase in maintenance expense; and environmental and even social problems.

Granular fertilizer products and mixed fertilizers are transported by trucks, railways, and ships, in bags and in bulk, and they are stored in bins and warehouses. Corrosion of vehicles and storage structures may result from absorption of water by the fertilizers in humid climates and from wetting by rain.

Agricultural machinery used for application of fertilizers in the field usually is fabricated of carbon steel which is protected by paint or organic coatings. These protective coatings may deteriorate from attack by acidic or basic fertilizers, and this leads to further corrosion of the then unprotected areas of the steel equipment.

The corrosive characteristics of fertilizer intermediates and products may be determined by simple and rapid laboratory tests that are based on accepted techniques and standard methods. The data obtained will be useful in extending the life of equipment used in industrial operations.

A sound knowledge of corrosion problems in the fertilizer industry is necessary for the development of efficient, practicable methods for control and selection of materials of construction that will reduce the expense of maintenance of the equipment and facilities.

CHAPTER 1

Corrosion Fundamentals

Corrosion is the deterioration of a metal or other material resulting from its interaction with the environment; this deterioration can occur by dissolution in liquid media or by oxidation at elevated temperature.

Corrosion science is concerned with the study of the causes and mechanisms of a corrosion process and the laws that govern them. Corrosion engineering applies scientific knowledge to the abatement of corrosion by practical and economical means. The study of corrosion is a highly interdisciplinary activity and involves knowledge of metal composition and structure, the nature of metal surfaces, the chemical and physical properties of the environment to which the metal is exposed, and the nature of the corrosion products formed, including thin films.

Corrosion increases costs and generates problems in many industries, including the fertilizer industry. In a recent report it was estimated that the cost of corrosion in the United States in 1975 was about $70,000 million which is about 4% of the U.S. gross national product.[1]

To control corrosion and so reduce its cost, much effort is devoted to three main activities:

1. Research on the causes and mechanism of corrosion;
2. Preventive control to prevent, delay, or minimize corrosion; and
3. Curative control to remedy corrosion after it has occurred.

The Electrochemical Nature of Corrosion

Most corrosion reactions, especially those occurring in aqueous media such as fertilizer solutions, are electrochemical processes.

The overall corrosion process is the combination of two reactions, anodic and cathodic, that take place at the metal-environment interface.

The anodic process or the oxidation of the metal is indicated by an increase in valence of the metal or the production of electrons.

---

1. "Economic Effects of Metallic Corrosion in the United States." A report to the Congress by the National Bureau of Standards, United States Department of Commerce, March 1978.

$$\underset{\text{metal}}{M} \rightarrow \underset{\text{cation}}{M^{+n}} + \underset{\text{electron}}{ne^-}$$

The cathodic process or the reduction of some species present in the electrolyte solution is indicated by a decrease in valence or the consumption of electrons. Several cathodic reactions often encountered in fertilizer solutions include:

Reduction of dissolved oxygen in aqueous media

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \text{ (neutral or basic solutions)}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \text{ (acid solution)}$$

Evolution of hydrogen

$$2H^+ + 2e^- \rightarrow H_2 \text{ (acid solution)}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \text{ (basic solution)}$$

Reduction of a metal in solution

$$Fe^{+3} + e^- \rightarrow Fe^{+2}$$

The overall corrosion reaction for iron in an acidic solution is a combination of dissolution of iron and evolution of hydrogen:

$$\begin{array}{ll} Fe \rightarrow Fe^{+2} + 2e^- & \text{Anodic reaction} \\ \underline{2H^+ + 2e^- \rightarrow H_2\uparrow} & \text{Cathodic reaction} \\ Fe + 2H^+ \rightarrow Fe^{+2} + H_2\uparrow & \text{Overall reaction} \end{array}$$

The overall corrosion reaction for iron in water is oxidation of iron to form a hydrated ferrous oxide or ferrous hydroxide which can be further oxidized in the presence of oxygen to ferric hydroxide, commonly known as rust:

$$\begin{array}{c} 2Fe \rightarrow 2Fe^{+2} + 4e^- \\ \underline{O_2 + 2H_2O + 4e^- \rightarrow 4OH} \\ 2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2 \end{array}$$

$$2Fe(OH)_2 + H_2O + \tfrac{1}{2}O_2 \rightarrow 2Fe(OH)_3$$

In the electrochemical process, the solid metal is oxidized to cations that go into solution at areas on the metal surface that act as anodes. The electrons liberated pass through the metal to surface

areas called cathodes, where they are removed by the reduction reaction and form corrosion products such as oxides, hydroxides, or salts. The rate and mechanism of a corrosion process are determined by the kinetic factors that govern the individual anodic and cathodic reactions, and the overall corrosion reaction is the sum of these individual reactions.

Potential, Current, and Resistivity

The potential of a pure metal, measured under defined conditions against a reference electrode, such as the standard hydrogen electrode (SHE), expresses its tendency to dissolve according to the reaction:

$$M \rightarrow M^{+n} + ne^{-} \qquad \text{Oxidation}$$

A second reaction occurs in this electrochemical cell:

$$2H^{+} + 2e \rightarrow H_2\uparrow \qquad \text{Reduction}$$

By convention the hydrogen reaction is assigned a standard half-cell potential of 0.000 volt.

These potentials are called standard oxidation-reduction potentials (redox potentials) because they are measured under standard conditions in which the ions M^{+n} and H^{+} are each present in the amount of 1 gram-atom/liter and at unit activity.

This cell may be described as follows:

$$M|M^{+n}(a=1)||H^{+}(a=1)|H_2(1\ atm)|Pt$$

The cell potential indicates whether the reaction may be spontaneous, according to the free energy equation:

$$\Delta G = -nFE$$

where

n is the number of electrons involved in the reaction

F is the Faraday constant, and

E is the cell potential.

In order for the reaction to proceed spontaneously it must have a negative free energy change, i.e., ΔG must be negative, and the cell potential must be positive.

Practical measurements of potentials of metals and alloys immersed in a given electrolyte solution are made against a stable reference electrode such as the standard calomel electrode (SCE) or the standard silver chloride electrode.

These potentials are arranged in a galvanic series that is used to predict the relative corrosion tendency of metals and alloys in a given environment, such as seawater or phosphoric acid. A metal or alloy may have different potentials depending on whether it is active or passive. Iron, chromium, titanium, nickel, and alloys containing them are examples. Passivation is generally associated with oxidizing media (high, positive potentials) and the formation of thin protective oxide films.

A short galvanic series, based on the potentials of metals and alloys in flowing seawater, at the velocity of 2.3 m/sec, is given in Table 1.

Table 1. Potential of Metals and Alloys in Flowing Seawater[a]

Metal/Alloy	Potential, Volt[b]
Anodic (Active)	
Zinc	1.03
Aluminum	0.79
Mild steel	0.61
AISI type 304 (active)	0.53
Copper	0.36
Admiralty brass	0.29
90/10 Cu/Ni	0.22
Monel alloy 400	0.11
AISI type 304 (passive)	0.08
Cathodic (Passive)	

a. Seawater velocity, 2.3 m/sec (7.8 ft/sec).
b. All values negative to SCE.

When a metal has come to equilibrium in its corrodent and is corroding freely, it will have a corrosion potential E_{corr} and a corrosion current-density i_{corr} between anode and cathode areas.

Corrosion potential (E_{corr}) can be easily measured experimentally. Corrosion current-density (i_{corr}) is usually determined indirectly because it is the current that flows between many small anode and cathode areas on the metal surface.

Corrosion current-density can be converted to a corrosion rate through the use of Faraday laws.

$$R_c = 0.13\ i_{corr}\ M/D$$

where

R_c is corrosion rate in mils/yr (mpy),

i_{corr} is current density in $\mu A/cm^2$,

M is the chemical equivalent weight of the metal in grams, and

D is the metal density in $grams/cm^3$.

Since most corrosion occurs in electrolyte solutions, it is customary to speak of the conductance, which is the reciprocal of the electrical resistance instead of the resistance of the solution. Corrosion is accelerated in aqueous solutions of such electrolytes as inorganic acids, bases, and salts since they conduct electricity to an extent depending on their degree of dissociation, as:

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$$

$$NaCl \rightleftarrows Na^+ + Cl^-$$

Values of electrolytic conductance of several electrolytic solutions are given in Table 2.

Table 2. Specific Conductance of Electrolytes in Aqueous Solutions

Electrolyte	Temperature, °C	Specific Conductance, mho. cm^{-1}
50% H_3PO_4	18	2.07×10^{-1}
85% H_3PO_4	18	7.80×10^{-2}
85% H_3PO_4	100	3.43×10^{-1}
50% H_2SO_4	18	5.41×10^{-1}
25% KOH	18	5.41×10^{-1}
5% $MgCl_2$	20	6.4×10^{-2}
20% $MgCl_2$	20	1.0×10^{-1}
Seawater	25	5.2×10^{-2}
Pure water	25	4.4×10^{-8}

For comparison, a current density of 1 $\mu A/cm^2$ corresponds to a corrosion rate of about 1 mpy for most metals. The exact

relationship between dissolution current density and corrosion rate should be calculated for each metal from Faraday's law. For instance, for the corrosion of iron expressed by the reaction:

$$Fe \rightarrow Fe^{+2} + 2e-$$

the relationship is:

$$R_c = 0.13i_{corr}\ (27.9/7.8)$$
$$= 0.465i_{corr}$$

so that R_c is 1 mpy when i_{corr} is 2.15 $\mu A/cm^2$

The potential may change as immersion continues, as a result of changes that occur on the metal surface or in the solution as the current flows from anode areas to cathode areas. This change is recorded as a curve of E versus time that indicates corrosion activity, passivity, breakdown of passivity, or passivation. These conditions are explained in the next section.

When an oxidizing agent is added to a corroding system that contains a nonpassivating metal, the corrosion rate increases and the corrosion potential shifts in the noble direction. The magnitude of these effects is dependent on the redox potential of the oxidizer and its kinetic parameters. Redox systems can be any typical oxidizing agent such as ferric, cupric, or chromate ion. On passive metals, oxidizers may affect the active-passive behavior as influenced by the chemical nature of the oxidizer, its interaction with the passive film, and its concentration.

The oxidizing power of a solution is measured with an inert electrode such as platinum against a half-cell such as a calomel electrode. The value obtained is called the redox potential of the solution, and its magnitude depends on the proportions of the oxidized and reduced species present in the electrolyte. This redox potential should not be confused with the standard redox potential of pure metals.

Redox potentials (on platinum) are often measured in electrolyte solutions, such as acids and fertilizer solutions, and also in soils to evaluate the oxidizing or reducing capacity of these media.

Polarization, Passivity, and Passivation

When a current flows between the cathodic and the anodic sites of a corroding metal, the potentials of both sites change and accordingly the potential of the metal changes. This change is termed "polarization," and it affects the rate of corrosion.

There are two different types of polarization, activation polarization and concentration polarization.

Activation polarization occurs during corrosion of metals in concentrated acid solutions. The reduction of hydrogen ion and the formation and evolution of hydrogen gas at the metal-electrolyte

interface cause a change of potential of the metal electrode. Accumulation of hydrogen gas then retards or polarizes the cathodic reaction. A species that accelerates hydrogen evolution, such as oxygen which combines with the hydrogen, depolarizes the cathodic reaction.

Concentration polarization refers to electrochemical reactions that are controlled by diffusion in the electrolyte. It occurs during corrosion processes in electrolytes that have low concentrations of reducible species such as oxygen in aerated water or hydrogen ion in dilute acids.

The total polarization of an electrode is the sum of the contributions of activation polarization and concentration polarization, which is called overvoltage because of its relation to the equilibrium potential.

Resistant metals and alloys that have zero or very low corrosion rates are used in fertilizer plants to avoid or minimize corrosion. Metals of this kind are said to be passive or to exhibit passivity. Passivation of a reactive metal requires the artificial creation of the passive state on its surface.

Metals that exhibit passivity are iron, chromium, nickel, titanium, and alloys of these metals. The passive condition in these metals is promoted by the presence in the electrolyte of oxidizing agents such as nitric acid, but halide ions tend to hinder passivation. The passivity of metals has been traced to the formation of oxide films on the surface of the metal. These films are very thin, only 30-100 Å thick; ordinarily they cannot be seen and they are not soluble.

Passivity is not a property of a metal itself, but it is assumed by certain metals in specific environments and under certain conditions. For instance, type 304 stainless steel is listed in Table 1 with a passive potential value of -0.08 volt in flowing seawater, but under reducing conditions which affect the passive layer the same metal may be active and have a potential value of -0.53 volt.

When a passive surface has been produced, it can often be maintained by conditions less stringent than those required to produce it. It can be maintained also artificially, as in anodic protection, by means of an external source of current at a more noble potential than its corrosion or open circuit potential.

Partial or complete breakdown of passivity, with consequent corrosion, may result from factors that partially or completely remove the passive film. Removal of the film can be effected by electrochemical reduction, by hydrogen evolved on the film, by chemical dissolution of the oxide film, or by mechanical damage resulting from bending, scratching, or impact. Under suitable chemical conditions in an appropriate environment, the damaged film can repair itself by a process called "self-healing."

Repassivated metals often have a better corrosion resistance than the same metal with a natural air-formed oxide film. Metals can be repassivated by treatment with oxidizing solutions such as concentrated nitric acid or mixtures of nitric acid and alkali metal bichromates.

The typical electrochemical behavior of a metal that undergoes an active-passive transition, illustrated by its anodic polarization, is shown as an "ideal" potential-current curve in Figure 1. Near the corrosion potential the metal dissolves at a rate that increases with increasing current density as the potential is raised to a value at which the current density abruptly decreases, indicating the beginning of the passive region. In this region, increase in the potential does not change the passive condition until a high potential is reached at which oxygen evolution begins and metal dissolves as higher-valence ions. This is the transpassive region.

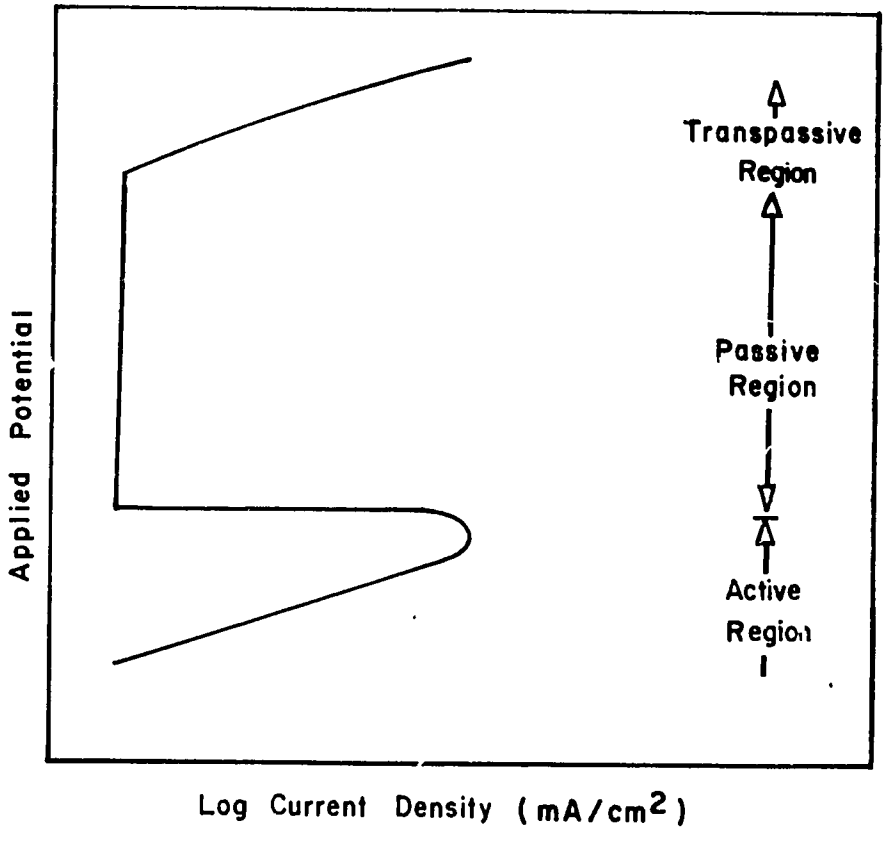


Figure 1. Anodic Polarization Curve Showing Three Regions of Corrosion Behavior.

These characteristics of the metal-environment system have been used to develop the method of anodic protection, to create new corrosion resistant alloys, and to study corrosion behavior by techniques that will be described in Chapter 6.

CHAPTER 2

Types of Corrosion

Corrosion can affect a metal in different ways that depend upon the nature of the environment and are reflected in the appearance of the corroded metal.

One method of classification of corrosion is based on the type of corrosion reactions and the characteristics of the environment involved. According to this approach corrosion is classified as wet or dry.

Wet corrosion occurs in aqueous solutions or in air in the presence of water vapor at ordinary temperature. Environments suitable for wet corrosion include natural waters, the atmosphere, soils, body fluids, and chemicals, in all of which hydrogen (H^+) and hydroxyl (OH^-) ions and dissolved oxygen (O_2) are necessary constituents.

The products of corrosion formed on the metal surface by reaction with water, acids, or alkalies include thin oxide films, hydrated oxides or hydroxides, and salts such as phosphates or sulfates, which may or may not be protective, depending on the physical and chemical properties of the products.

Dry corrosion results from reaction of metals with hot gases or vapors such as oxygen, halogens, hydrogen sulfide, and sulfur-containing gases. These reactions form thick oxides and result in scaling and tarnishing. Thus, oxidation by oxygen at high temperature is an electrochemical process in which the metal is oxidized and oxygen gas is reduced, resulting in the formation of an oxide scale that grows at the scale-oxygen interface by outward cation diffusion. The rate of oxidation then is expressed as a weight gain per unit area per unit time.

Dry corrosion occurs in gas turbines, rocket engines, heating furnaces, petroleum refining equipment, and steel plants.

On the basis of the appearance of the result of corrosion on the metal surface or in the geometry of the metal-environment system, corrosion can be classified as uniform or localized.

In uniform corrosion all the exposed metal surface corrodes at about the same rate, resulting in a uniform decrease in thickness of the metal. Uniform attack occurs when carbon steel is immersed in a mineral acid such as phosphoric acid and the steel dissolves at a uniform rate over its entire surface.

Most corrosion in industrial systems, such as chemical plant equipment, occurs at specific areas or parts of a piece of

equipment, indicating that corrosion is localized. Certain areas of the metal surface corrode at higher rates than others because of heterogeneities in the metal, in the environment, or in the geometry of the equipment, and often results in unexpected or premature failures.

Localized attack results from differences in aeration, concentration, temperature, velocity, and pH of the environment. Localized corrosion occurs as pits, crevices, cracks, grooves, and eroded areas.

The most common forms of localized corrosion, which are often encountered in the chemical process industry, are illustrated in Figure 2 and described in the next sections.

Galvanic Corrosion

Galvanic corrosion occurs when two dissimilar metals in direct electrical contact are exposed to a corrosive solution or atmosphere. Under these conditions, the potential difference between the metals produces a galvanic current that flows between them and results in corrosion of the more negative member of the bimetallic couple.

The galvanic series of metals and alloys in which metals are listed according to their corrosion potential, as illustrated in Table 1, indicates the relative corrosion tendency of coupled metals. The magnitude of the galvanic corrosion current depends on several factors such as the difference in corrosion potential, the products of the corrosion, and the ratio of the areas of the more active (anodic) and less active (cathodic) surfaces.

Galvanic corrosion is frequently encountered in fertilizer plants. When brass valves are placed in mild steel pipes, that carry water or chemicals, the mild steel corrodes adjacent to the brass valve. In this bimetallic couple of steel and brass, steel is the corroding, anodic metal and brass the protected cathodic metal. Similarly, coolers with copper or brass tubes in steel shells suffer from galvanic corrosion, and the steel corrodes at the junctions of the metals as above.

Sometimes the polarity of a galvanic couple is reversed during service as with the zinc-iron couple, in which the zinc normally corrodes. However, when the temperature is raised above 60°C, the iron becomes anodic to zinc in certain waters, and the iron corrodes. This reversal has been attributed to the formation of a protective zinc oxide film, and at the higher temperature the film is noble to steel.

Galvanic corrosion can be avoided or minimized by electrical insulation with nonconducting plastics or rubbers between dissimilar metals by selecting a combination of metals as close as possible

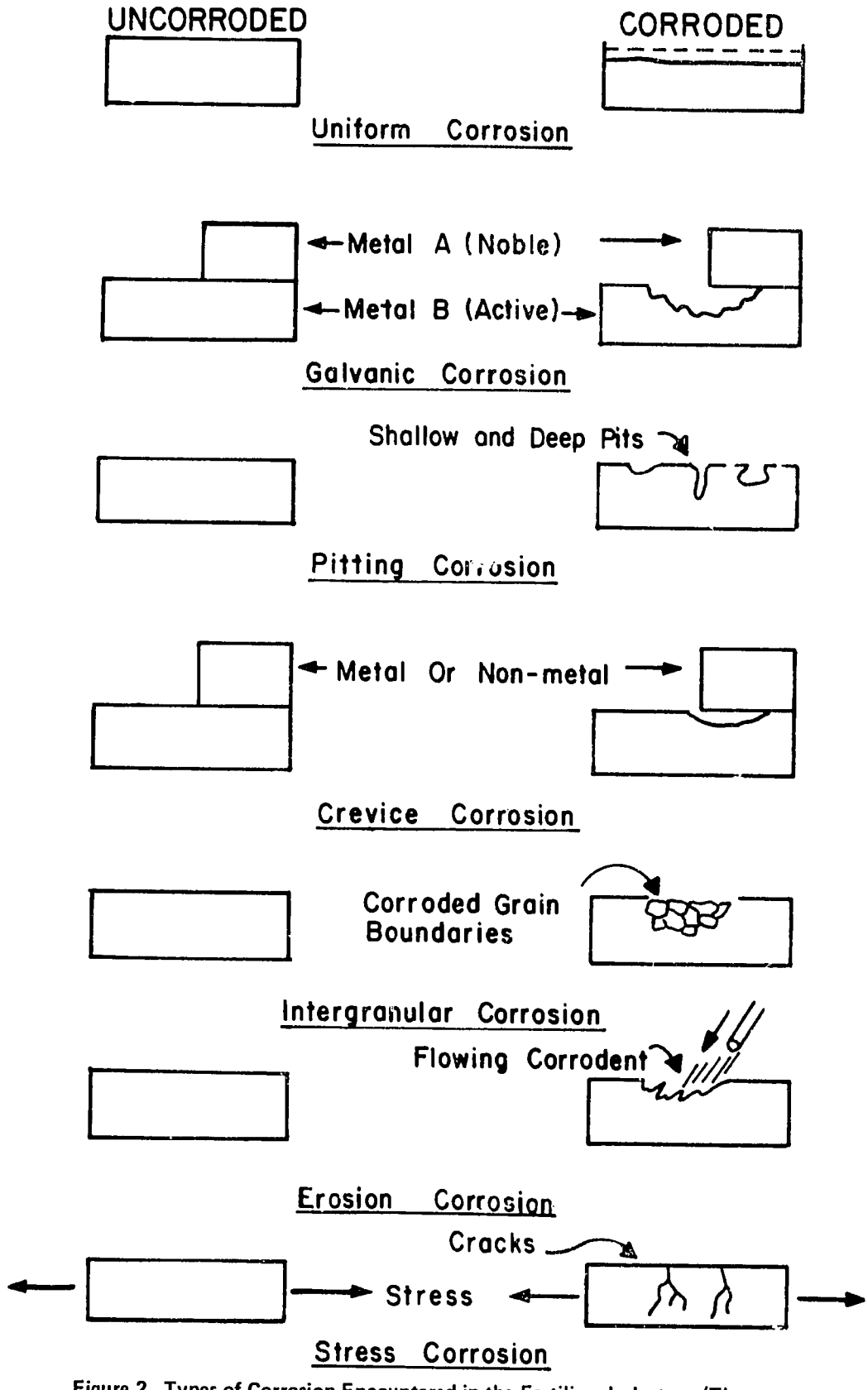


Figure 2. Types of Corrosion Encountered in the Fertilizer Industry. (The upper surfaces of the material are in contact with the corrodent.)

in the galvanic series and by applying coatings and paints to the metals for protection from atmospheres or liquids to which they are exposed.

Crevice Corrosion

Intense localized corrosion often occurs within narrow crevices formed by riveted plates or by contact of metals with nonmetallic solids such as plastic and rubber gaskets, and under deposits of sand, scale, corrosion products, or dirt. This phenomenon, which is called crevice corrosion, results from changes in the electrolyte solution within the crevice and that adjacent to it. Changes in dissolved oxygen content, in concentration of metal chloride, or in pH cause the formation of anodic-cathodic corrosion cells in which the anodic portion corrodes, and the rest of the surface suffers little or no damage.

Stainless steels are particularly subject to crevice corrosion, but improper geometrical configurations cause many metallic materials to suffer from this type of corrosion.

The obvious method of controlling crevice corrosion is to eliminate crevices in the design of the equipment and to avoid geometrical conditions that allow the formation of deposits on the metal surface.

Pitting Corrosion

Pitting corrosion results from highly localized attack that forms pits in the metal surface. It leads to premature failure of the equipment by perforation and consequent leakage of fluid.

Pitting occurs frequently in environments that contain aggressive ions such as chloride. Typical pitting occurs on 18/8 stainless steels (American Iron and Steel Institute [AISI] type 304) exposed to stagnant metal halide brines or seawater and in copper pipes carrying hot water, even those containing only small amounts of chloride.

Passive metals and alloys, whose natural potentials are in the passive region, are pitted when the redox potential of the solution exceeds a certain critical value; the passive condition then is destroyed and pits form. The potentiostat is useful in studies of the formation and mechanism of pitting. The process occurring within a corrosion pit leads to a lowering of pH and an increase in the content of aggressive ions such as Cl^-, both of which accelerate the corrosion process and the growth of pits.

To prevent pitting in chemical equipment used in fertilizer plants, the equipment should be fabricated from metals with homogeneous, smooth, and clean surfaces. Surface cleanliness, attained by avoiding deposits of dirt or biological growths such as algae, helps to avoid pitting.

Intergranular Corrosion

Metals and alloys have a crystalline structure in which atoms are arranged as grains with grain boundaries between them. These grain boundaries are areas of mismatch between grains in some metals and alloys, and they sometimes exhibit high chemical activity. Intergranular corrosion occurs along these grain-boundaries, much as it does in metallographic etching. Intergranular corrosion may be caused by impurities at the grain boundaries or by depletion of one of the alloying elements in or adjacent to the grain-boundary areas. In 18/8 stainless steel, which has a maximum carbon content of 0.08% when heated to the sensitizing temperature, the chromium (Cr) combines with the carbon to precipitate chromium carbides, thereby depleting chromium in the zone near the grain-boundaries, and these zones of low chromium content are corroded preferentially. Austenitic stainless steels are subject to intergranular corrosion when they are heated in the range 510°-790°C. Typical intergranular corrosion is shown in Figure 3.

Figure 3. Intergranular Corrosion of Durimet 20 Exposed to Wet-Process Phosphoric Acid—Result of Improper Heat Treatment of the Impeller (250X).

To avoid intergranular corrosion in equipment constructed of austenitic stainless steels, they should be properly heat-treated after fabrication, or the carbon content should be below 0.03% as in so-called "low carbon" stainless steels, such as 304L. Special stainless steels that contain strong carbide formers or stabilizers such as titanium (type 321) or columbium (type 347) are particularly resistant to intergranular corrosion.

Erosion Corrosion

Erosion corrosion occurs in many liquid or gaseous flow systems in either the presence or absence of solid particles. Erosion corrosion is common in slurries, as the result of the synergetic action of mechanical erosion and electrochemical corrosion by a moving fluid that contains both corrosive species and suspended erosive solid particles. This type of erosion corrosion is a frequent problem in chemical process plants that handle corrosive slurries such as those in the digesters of WPA plants.

The erosion effect in an agitated chemical reactor handling a solid-liquid reaction is governed by many factors, including the density, hardness, shape, size, and size distribution of the solid particles; the density and kinematic viscosity of the slurry; the type of flow (laminar or turbulent); and the velocity. High flow velocities, turbulence, and impingement lead to mechanical damage and may remove the air-formed protective oxide film on passive alloys. Adherent solid corrosion products, such as metallic phosphates or sulfates which form a protective layer under stagnant conditions, are swept mechanically from the steel surface by high fluid velocities, and combinations of these actions can result in accelerated, catastrophic attack.

Many metals and alloys, such as stainless steel, aluminum, and lead, are susceptible to erosion corrosion. All types of equipment that handle moving fluids in fertilizer plants, such as reactors, pumps, centrifuges, impellers, agitators, pipes, and nozzles are apt to undergo erosion corrosion. The attack is characterized by the formation of grooves or rounded depressions with a directional pattern that usually is related to the direction of the fluid flow.

Methods for controlling erosion corrosion include the use of alloys with high resistance to erosion corrosion because of their hardness, application of resilient coatings, and modifications in the design and geometry of the equipment. Damaged stainless-steel impellers may be repaired by weld-filling, polishing, and passivation in oxidizing solutions.

Stress Corrosion Cracking

Stress corrosion cracking (SCC) is the cracking of metal in a corrosive environment, under a considerable tensile stress, either residual from heat treatment or fabrication or from cyclic stresses applied during operation of the equipment. The continued action of tensile stress and corrodent may result in cracking of the metal; the cracking can be either transgranular or intergranular or a mixture of both.

The overall stress-corrosion process comprises an induction period in which cracks are initiated by corrosion damage, followed by propagation of these cracks by a joint electrochemical-mechanical mechanism until failure is complete.

Failure by SCC is frequently met in fertilizer plants. Copper-base alloys crack frequently in ammonia and ammonium salts, carbon steel cracks in caustic soda solutions and ammonium nitrate solutions, and austenitic stainless steels crack in hot, concentrated chloride solutions such as those of magnesium chloride. Stress corrosion cracking can be prevented or minimized by several techniques, including reducing stress of the metal by proper heat treatment, avoiding chloride solutions, removing oxygen from chloride-containing solutions, applying cathodic protection, using corrosion inhibitors when feasible, or selecting cracking-resistant alloys otherwise suitable for the intended purpose.

CHAPTER 3

Corrosion Protection and Control

The chemical industry deals with the production and handling of chemicals; it comprises a wide spectrum of industries such as fertilizers, pulp and paper, petroleum refining, metal extraction, petrochemicals, and textiles. These industries have a high level of corrosion risk resulting from several common characteristics:

1. They handle and process corrosive acids such as nitric, hydrochloric, sulfuric, and phosphoric.

2. They operate under severe hydrodynamic conditions that include reaction, distillation, agitation, circulation, and high flow velocities.

3. They operate at relatively elevated temperatures to accelerate the chemical reactions.

All these conditions require the application of corrosion-control methods and techniques from the early stages of design through the construction, erection, and operation of the plant. The simplest way to prevent corrosion of a metal that is not resistant to its environment is to form on the metal surface an impermeable, physical barrier that excludes the environment. Other methods involve modifications of the metal or the corrodent or both.

Practical methods that minimize or eliminate corrosion include selection of resistant materials of construction and application of coatings to protect the underlying material. Remedial measures for treatment of corrosion after it has appeared include change of material, repair of equipment, installation of new protection systems, and alteration of the process conditions.

Materials Selection

Use of corrosion-resistant construction materials is the most direct means of preventing corrosion. Corrosion resistance is the main property to be considered in the choice of materials for chemical plant construction, but the final selection must be a compromise between technological and economic factors. It is sometimes more economical to use a high-priced corrosion-resistant material that will provide long and trouble-free service than to use a lower priced material that may require frequent maintenance or replacement.

The technical process of selection can be divided into three main stages:

1. Analysis of the requirements and collection of the relevant information. The conditions imposed by the chemical process and the corrosion resistance required by the plant are evaluated in this first stage. Information on resistance of materials of construction to corrosion by industrial chemicals is available in many source books, publications of standards organizations, and promotional literature supplied by manufacturers. A number of these sources are listed in Appendix D.

2. Selection and evaluation of candidate materials. A wide variety of materials is available to the plant designer. These materials include metals and alloys, plastics, rubber, paints, ceramics and refractories, carbon, and graphite. A preliminary screening is based on the information collected during the first stage. The suitability of possible materials, based on their availability, strength, ease of fabrication, maintenance, safety, and cost, is critically evaluated.

3. Selection of the most suitable material. The material finally selected should be suitable to the environment and conditions to be imposed in the plant and should be able to perform its function safely for a reasonable period of time at a reasonable cost.

Coatings and Linings

The purpose of a coating or a lining is to act as a nonreactive barrier between the environment and the material to be protected. A technical differentiation is made between a coating that is less than 1 mm thick and is used for exposure to an atmosphere and a lining that may be 1-3 mm thick and is used for exposure to liquids.

While coatings usually are applied as a liquid or a powder or deposited from a solution, linings are applied as solid materials such as sheets of rubber. Some linings are in the form of acid-resistant bricks, and others are polyester or epoxy resins reinforced with glass flakes or fibers. A great variety of coatings is available. Several types are resistant to chemicals and are used in chemical and fertilizer plants and equipment. Coatings and linings fall into three main groups, based on their chemical nature: metallic; organic, including paints; and inorganic, including conversion and anodic coatings.

Relatively thin metallic coatings are applied by hot dipping in molten metal as in the zinc coating of steel to prepare galvanized steel or by electroplating of a thin layer of metal from an electrolyte as in chromium- or nickel-plated steels.

Cladding is a technique in which a thin sheet of a corrosion-resistant metal or alloy such as titanium or stainless steel is applied on a strong and cheap metal such as carbon steel. The two metals are bonded by hot rolling or through use of explosive energy.

Organic coatings, including paints, are used primarily to protect structural steelwork, agricultural equipment, and packing and storage facilities against corrosion from exposure to the atmosphere, soil, and water.

Paints are complex mixtures that are applied as a liquid film on a surface and harden to a solid protective coating. To protect against corrosion, a paint coating should exhibit good cohesion and adhesion, low permeability to air and moisture, and high chemical resistance.

To ensure the success of a coating, the surface of the material to be protected should be properly cleaned before application of the coating. Suitable chemical and mechanical pretreatments are specified in codes of practice issued by the Steel Structures Paint Council (SSPC), the Swedish Institute of Standards (SIS), National Association of Corrosion Engineers (NACE), and other technical organizations.

Porcelain enamels and glass are inorganic coatings that withstand a wide variety of chemicals.

Chemical conversion coatings are inorganic compounds such as phosphates or chromates. These are formed by exposing the metal to a phosphoric acid or chromic acid bath.

Anodizing involves the conversion of the metallic surface to an oxide. Aluminum is covered by a thin film of aluminum oxide (Al_2O_3) by electrolytic anodic oxidation in a bath of sulfuric acid to increase its resistance to atmospheric corrosion.

Cathodic and Anodic Protection

Corrosion of a metal in solution is generally an electrochemical process that occurs at a certain potential at which an electrical current flows between anodic and cathodic areas of the metallic system. Thus, it is possible to decrease or prevent this corrosion by applying a potential that controls the direction and magnitude of the current. Electrical protection methods include

cathodic protection, anodic protection, combination of cathodic and anodic protection, and modification to make the environment less aggressive to the metal.

It is often more economical to provide protection against corrosion by improved design that anticipates corrosion than by application of control methods after corrosion has occurred. Proper design of process equipment and plant, based on thorough knowledge of corrosion fundamentals, can prevent or minimize difficulties with corrosion. The selection of the optimum solution to corrosion problems should be based, not only on knowledge of corrosion technology, but also on an economic evaluation of a corrosion control system and its maintenance.

Monitoring of corrosion in operating chemical plants includes both visual inspection of open equipment during shutdown, that should be planned at regular intervals, and installation of devices that will detect the onset of conditions when corrosion could become serious. A number of such devices are now in use, such as sentinel holes in pipes, weight-loss coupons exposed in vessels, and electrical instrumentation that detects changes in corrosion potential. The electric current imposed to maintain the cathodic state of the protected metal can be supplied or "impressed" from an outside direct-current source, such as a battery or a rectifier that converts alternating current to direct current. It can also be supplied by a more active metal that corrodes in preference to the metal being protected. More active metals, such as zinc, magnesium, and aluminum, are called sacrificial anodes since they are destroyed during the protection process and must be replaced periodically to maintain the integrity of the systems.

Magnitude of protective currents and potentials are determined empirically. To protect a steel structure buried in a corrosive soil, the steel is polarized to a potential of -0.85 volt versus a copper/copper sulfate reference electrode, and current densities of 1-5 mA/ft^2 (about 1-5 $\mu A/cm^2$) are required for full protection. Protection of steel in chemical process equipment and in salt brines requires a current density of 10-15 mA/ft^2 for bare steel surfaces. Application of cathodic protection in the chemical process industry usually requires laboratory development and plant control, but it may provide an economic solution to costly corrosion problems.

Cathodic protection can be applied only in the presence of an electrolyte and is, therefore, used for steel immersed in water or in contact with chemicals or fertilizers in transport and storage equipment. Cathodic protection systems are used to prevent the corrosion of ships, underground pipelines, tanks for storage of water and chemicals, heat exchangers, and structures standing or floating in water. Protection is also applied to structures buried in corrosive soils that have relatively low resistivity.

Sacrificial anodes of zinc, magnesium, or aluminum and their alloys are commonly used in the cathodic protection of ships, pilings, and buoys; impressed-current systems are used to protect long underground oil, gas, and water lines.

Anodic protection lowers the rate of corrosion of immersed metals and alloys by controlled anodic polarization that induces passivity. It is based on the formation of a protective film on the metallic surface by an externally applied anodic current. It is applicable to metal-electrolyte solution systems in which passivity can be established and maintained.

Since the potential is the critical factor in anodic protection, a reference electrode and a potentiostat are required to maintain the desired potential automatically by increasing or decreasing the applied anodic current. The initial anodic current density required to initiate the protection may be quite high, in the region of several mA/cm^2, but once passivity is established the current density necessary to maintain the passive state can be very low, in the region of several $\mu A/cm^2$.

The effectiveness of anodic protection in chemical process systems depends upon the composition, concentration, purity, temperature, and degree of agitation of the electrolyte solution concerned. Corrosive impurities, particularly halogen ions in sulfuric and phosphoric acid, made anodic protection difficult because they interfere with the formation and maintenance of the passive state.

Anodic protection is widely used in the chemical and fertilizer industries, particularly in the United States. It has been used to protect large mild steel vessels containing sulfuric acid, stainless-steel tanks for storage and road and rail transport of phosphoric acid, mild steel tanks for storage and transport of nitrogen fertilizers, and steel vessels for storage of ammonium carbonate/ammonium nitrate solutions.

Anodic protection lowers the rate of corrosion of stainless steel in phosphoric acid and so decreases the formation and accumulation of hydrogen in stainless steel vessels, which has been reported as the cause of explosions in phosphoric acid tanks.[2]

Inhibitors

Corrosion can be controlled also by modifying the environment by neutralizing or removing corrosive agents. Dissolved oxygen, the main corrosive factor in water and aqueous salt solutions, can

2. Lowe, J. B. 1961. "Corrosion-Generated Hydrogen Explodes in Phosphoric Acid Tank," Corrosion, 17(3):30.

be removed by reaction with sodium sulfite (Na_2SO_3) or hydrazine (N_2H_4) or by physical means such as deareation under vacuum or raising the temperature.

An additional method of modifying the corrosion characteristics of the environment is addition of inhibitors. Corrosion inhibitors are substances that slow the rate of corrosion reactions when added in relatively small amounts to the corrosive environment. Inhibitors are divided into four groups:

1. Anodic inhibitors which retard the anodic corrosion reaction. They are usually either oxidizing agents such as chromates and nitrates that promote passivity or film formers that precipitate insoluble films, such as alkalies, phosphates, and silicates on the anode areas.

2. Cathodic inhibitors that repress the corrosion reaction, such as reduction of oxygen in near-neutral solutions or evolution of hydrogen in acid solutions. They include oxygen scavengers, such as sodium sulfite and hydrazine, and hydrogen evolution poisons, such as ions of arsenic and antimony.

3. Adsorption inhibitors which are adsorbed on the surface of the material and form a thin protective film that suppresses dissolution of metal, reduction of oxygen, or evolution of hydrogen. Most are organic substances such as amines, aldehydes, oils, and waxes, that have a polar group and adsorb on the surface of the metal to be protected.

4. Vapor-phase inhibitors which are organic substances that volatilize slowly and condense on the metal surface. They protect steel machinery or parts from rusting during shipment and storage. Typical examples are amine salts, morpholine, and sodium benzoate.

Inhibitors are successfully used for the control of corrosion of mild steel in cooling water systems, in central heating systems, and in steam condensate lines. In nitrogen fertilizer solutions of the NH_4NO_3-NH_3-H_2O type, corrosion of steel has been prevented by addition of 500 ppm of thiourea or $(NH_4)_2HPO_4$. The oil industry uses inhibitors to control corrosion at every stage of production from initial extraction to refining and storage.

Economic considerations are of the utmost importance in anticorrosion methods involving inhibitors. The cost of an inhibitor under operating conditions is determined largely by both its chemical stability and its efficiency as an anticorrosion agent.

CHAPTER 4

Corrosion Testing

Corrosion tests are made in the service of different industries, such as chemical, petroleum, automotive, and steel, and for a variety of reasons such as selection of materials of construction, monitoring plant corrosion, prediction of service life of equipment, development of corrosion-resistant alloys, and study of corrosion mechanisms. The methods and techniques used in these tests are shown in Appendix A. Well-planned and executed tests should yield reliable and reproducible results. The interpretation of these results and their application for practical industrial purposes are the most important aspects of corrosion testing. Sources of information on corrosion control and testing are shown in Appendix B.

Corrosion tests for industrial purposes should simulate plant or field conditions as closely as possible. Accelerated tests require magnification of the effect of factors such as temperature and velocity of the corrosive fluid with respect to the test specimen. Such tests are intended to produce in a short time the degree and type of corrosion that would occur in a much longer time in service. The results of these tests, however, are sometimes difficult to interpret.

The main purposes of corrosion testing in the fertilizer industry are:

1. Determination of the corrosion characteristics of commercial fertilizers so that methods of minimizing or avoiding corrosion of equipment during storage, transportation, and field applications can be devised. A list of some of the more common intermediates and fertilizer products is shown in Appendix C.

2. Evaluation and selection of materials for a specific fertilizer process or a new or modified fertilizer plant that will withstand corrosion better than materials being used in established plants. Sources of information on corrosion resistance of materials of construction are shown in Appendix D.

3. Study of the mechanism of corrosion by fertilizer intermediates and products, including the effects of impurities contained in the raw materials from which the fertilizer is produced.

4. Development of research and test methods and techniques designed specifically for study of corrosion in fertilizer systems. Some pertinent literature references for such a study are given in Appendix E.

A brief list of instruments and equipment for a corrosion laboratory to be set up in a fertilizer production complex or a fertilizer research organization, is presented in Appendix F. These instruments are used in laboratory and plant corrosion testing and in plant corrosion control.

Simulation of Industrial Conditions

To obtain reliable results, corrosion tests in the service of the fertilizer industry should be made under conditions that simulate the actual industrial conditions as closely as possible. The process variables and the plant operating conditions should be duplicated as far as possible, with allowance for differences in size and volume that are inherent in the laboratory or pilot-plant conditions. The greater the deviation from plant conditions the less reliable will be the results of the test.

The more common process and plant variables that influence corrosion and that have to be simulated in corrosion tests are discussed below.

Concentration of Major Constituents--The rate of corrosion of a metal may vary with the concentration of the corrosive agent and depends on both its chemical nature and the properties of the corrosion products formed on the metal surface. For instance, in hydrochloric acid solutions the corrosion rate increases with increase in concentration of the acid. With mild steel immersed in phosphoric or sulfuric acid, however, the corrosion rate may decrease with increasing concentration of acid because of the formation of a protective layer of iron phosphate or sulfate that is insoluble in the concentrated acid. In sulfuric acid the hydrogen ion concentration increases to a maximum with increase in concentration to about 50% above which it decreases, so that corrosion rate of iron or steel is highest at a sulfuric acid concentration of about 50%, and decreases with increase in acid concentration.

The rate of corrosion of carbon steel and cast iron in brines decreases with increasing salt concentration because of the resultant decrease in dissolved oxygen, which is the main corrosion factor in these environments.

Effects of Impurities--The impurities present in a fertilizer raw material, such as phosphate rock or sulfuric acid, or in a commercial fertilizer may affect the corrosion behavior of a metal or alloy, depending on the chemical nature and activity and concentration of the impurity in the fertilizer system. An impurity may act as a corrosion accelerator, as do chloride ions in WPA, or as a passivator as do nitrate and cupric ions in the production of WPA. Some impurities may lower the corrosion rate by reacting with a highly corrosive component of the system, as does active silica in its reaction with hydrofluoric acid in the production of WPA.

Other impurities may accelerate corrosion by forming soluble complexes with the metal. An example is the dissolution of copper or copper alloys as copper ammonia complexes when ammonia, in the presence of oxygen, appears as an impurity in a commercial fertilizer.

The effects of impurities are often complex. The first step in dealing with impurities is identifying them, determining their amounts, and locating their source. Synthetic solutions containing different concentrations of impurities may be used for studying the influence of the impurities on the corrosion process and its rate.

Influence of pH--Many alloys, especially ferrous alloys such as steels, are vigorously attacked in acidic media with marked evolution of hydrogen gas; pH is therefore an important factor in corrosion control and corrosion testing.

Granulated fertilizers may be acidic, neutral, or basic, and may dissolve and undergo hydrolytic decomposition in contact with moisture, thereby liberating hydrogen or hydroxyl ions that affect the corrosion resistance of the steel equipment used for storage, transportation, or field application of the fertilizer.

Liquid or solution fertilizers contain different amounts of ammonia, phosphoric acid, potassium chloride, urea, and ammonium nitrate. The corrosion behavior of different metals such as steel, aluminum, and copper alloys will depend on the pH of these fertilizer solutions and on the properties of the corrosion products formed on the metal and on the reactivity of the metal at a given pH and chemical composition of the solution.

In industrial waters, such as cooling water used in fertilizer plants, the pH of the water may affect the formation of scale on steel equipment surfaces and thereby alter the protective characteristics of the scale.

The pH of a fertilizer test solution and its change with time because of hydrolysis or other chemical effects should be measured before, during, and after the corrosion test.

Influence of Temperature--Rise in temperature increases the rate of almost all chemical reactions. The effect of a temperature rise on a corrosion rate is complex and depends on whether the metal is active or passive and on the chemical nature of the environment.

In nonoxidizing mineral acids, such as phosphoric acid, the corrosion rate increases with rise in temperature. On the other hand, a small rise in temperature of an oxidizing acid such as concentrated nitric acid increases the corrosion resistance of

passive stainless steels, because of the increase in the oxidizing power of the acid.

In waters, whether potable or industrial, the major factor controlling corrosion is dissolved oxygen, and a rise in temperature to near the boiling point may lead to a decrease in corrosion rate because of the lower oxygen content of the hot water.

In equipment used for heat transfer, the temperature of the metal may affect the rate of corrosion of the metal surface or the conditions of formation of the scale and hence the corrosion resistance of the metallic surface. Electronic, thermostatically controlled devices are recommended for maintaining constant or regularly fluctuating temperatures.

Effects of Velocity--The effects of the velocity of a corroding fluid are, like those of temperature, complex and dependent on the characteristics of the metal and the environment and their interaction. Vigorous agitation or high fluid velocity affects the corrosion behavior of the metal surface by accelerating the diffusion of the ionic species involved in the activation or concentration polarization reactions. Mechanical damage or removal of such corrosion products as passive films or scale at high fluid velocities results in accelerated attack of the metal.

High-velocity process streams that contain hard solid particles in suspension, such as those formed in WPA production, cause erosion-corrosion damage to metal agitators or impingement corrosion in pipeline bends.

Procedures and apparatuses for conducting controlled velocity corrosion tests in the laboratory are described in NACE test method TM-02-70. Other devices for studying corrosion in recirculating fluids including erosion corrosion are the loop test and specially designed laboratory equipment (see Appendix F).

Effect of Aeration--Aeration, or the supply and presence of dissolved oxygen from air in a liquid environment, may have an important effect on corrosion behavior. Some metals and alloys are more rapidly attacked, and others are more resistant to corrosion in the presence of oxygen, depending on whether the metals are active or passive and on the stability of the passive films in the particular environment. Effects of aeration on corrosion are observed in pumps and pipelines that handle acids, in the liquid lines of tanks, and in crevices or under deposits on metal surfaces.

Aeration is simulated by bubbling air or oxygen through the test solution, and the degree of aeration should be measured. If complete deaeration is desired, then nitrogen or argon should be bubbled through the solution. Tests conducted in vessels open

to the air with agitation or circulation of the liquid are considered to be air-saturated.

Techniques for aeration and deaeration are described in standards ASTM G31-72 and NACE TM-01-69 and TM-02-70.

Types of Corrosion Testing

Corrosion testing in the service of the chemical and fertilizer industry may consist of four phases which sometimes may be carried out on the following logical sequence.

Laboratory Tests--These tests are characterized by small specimens and small volumes of solution and by use of laboratory measuring instruments. These tests have several purposes--determination of corrosive properties of chemicals and fertilizers, selection of alloys for chemical plant equipment, and identification of corrosion mechanisms.

Pilot-Plant Tests--These tests are made in small-scale plants that duplicate the intended industrial plant operation. Test specimens can be exposed in the pilot plant, and the corrosion behavior of the equipment itself is observed. Corrosion attack may be detected by determination of metallic ions in the process liquor, before and after contact with the metallic equipment. It should be borne in mind, however, that the corrosion data obtained are dependent upon the pilot-plant operating conditions--actual raw materials, temperatures, concentrations and velocities of process fluids, aeration, presence of corrosive impurities, etc.--and may differ somewhat from those produced in the full-scale plant.

Industrial Plant Tests--The tests are carried out by exposure of equipment and test specimens to actual service conditions. They are used to study corrosion behavior of existing materials when process conditions are changed or to evaluate and select materials of contruction that are less expensive or have better corrosion resistance.

Field Tests--These involve different types of tests that are related to the application of fertilizers in the field by agricultural machinery. They are used to study corrosion by soil, the effect of atmospheric exposure on painted or coated steels, and the effect of atmospheric polluting agents on corrosion of the equipment. Field tests require a large number of specimens and special exposure devices and should be made at several geographical locations to determine the effects of different soil or field conditions.

The scientists and engineers involved in research, development, and application of fertilizers should be concerned, at an early stage of their work, with the response to corrosion of the

construction materials of equipment used for production, storage, transportation, and field application of fertilizers. Simple and rapid laboratory tests can be made and pilot-plant experiments may be utilized to collect corrosion data that will help to avoid failure of equipment due to corrosion. To attain this end, a close and effective cooperation should be established between the research and development personnel and those studying corrosion aspects of fertilizers.

CHAPTER 5

Weight-Loss Techniques

Weight-loss tests are the most common and simplest of all corrosion tests. A clean specimen is measured and weighed, exposed to the corrodent for a measured time, removed, cleaned to remove corrosion products, and reweighed; the corrosion behavior and corrosion rate are evaluated from the loss in weight.

This technique is described in standards NACE TM-01-69 and ASTM G31-72 (Appendix G). The recommended procedures might not be followed strictly, but they should be adapted to the process or plant conditions and to the particular purpose of the test.

A procedure for a short and simple laboratory corrosion test is presented in Appendix H.

Specimen Preparation

The tests should be made on available materials on which complete information is also available as to their chemical composition, fabrication, metallurgical history, and commercial identification. If this information on a material is incomplete, the data obtained with it will be of little practical use.

The size and shape of the specimens will vary with the purpose of the test, the nature of the material, and the apparatus to be used. The specimens may be circular, square, cylindrical, or rectangular, and they usually are cut from thin rolled sheets, from extruded or cast rods, or from cast pieces. Thin specimens are preferred because they are easily prepared, and they expose minimum areas of cut edges. Primarily, specimens that are 1/16 to 1/8 in (1.66-3.2 mm) thick, 1 in (25.4 mm) wide, and 2 in (50.8 mm) long are used in laboratory tests, but plant- and field-test specimens usually are larger, depending on the test conditions (Figure 4).

Surface preparation varies with the purpose of the test. Tests for selection of materials for fertilizer plant equipment should be made with specimens with the same surface as that of the material to be used in the plant. This surface is sometimes called the "as received" condition, which for stainless steel would be a mill-finish grade "2D" or "2B."

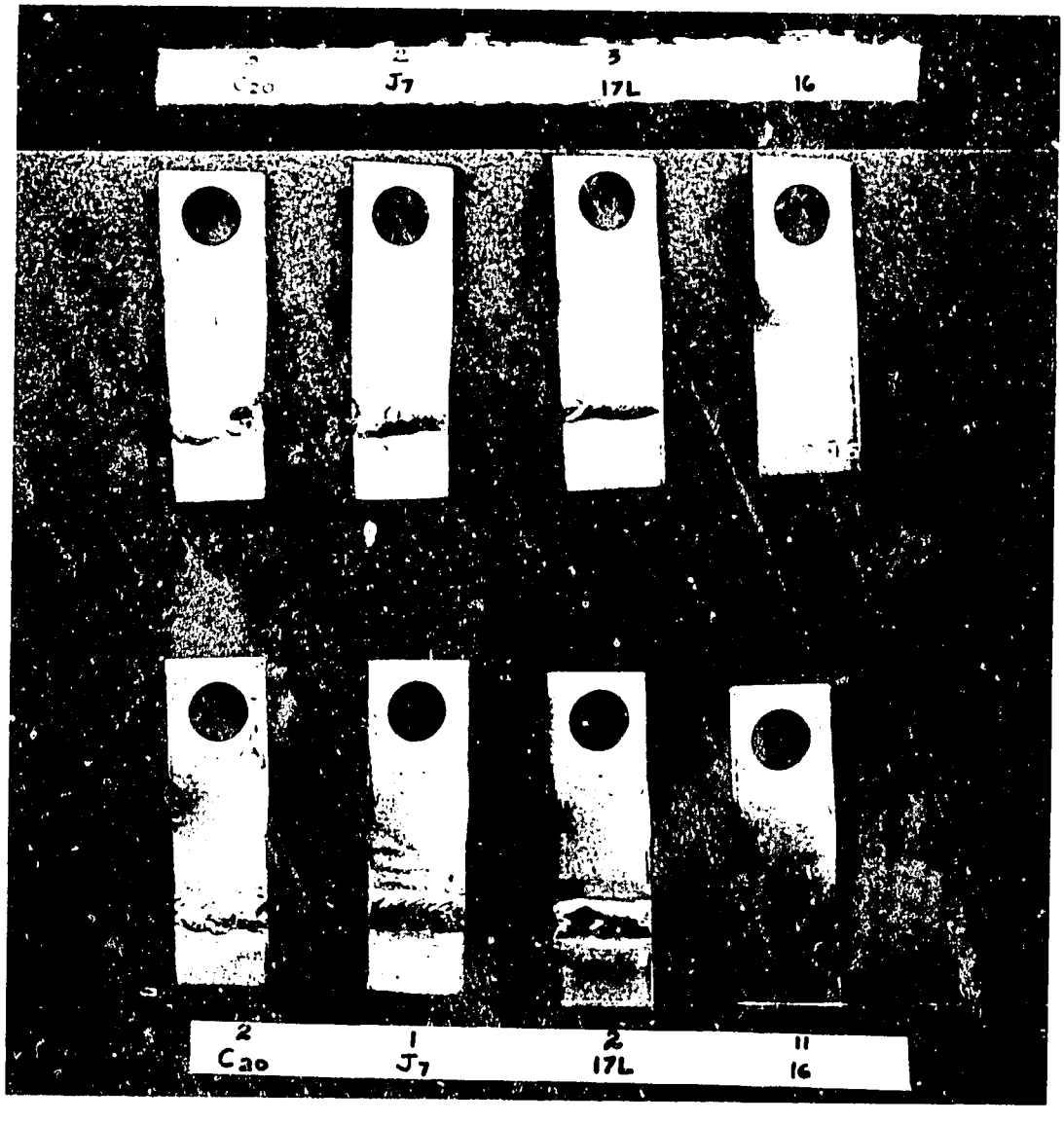


Figure 4. Typical Corrosion Specimens Before Exposure to Corrodents.

A widely used surface finish is produced by mechanical polishing with No. 120 abrasive paper or cloth. Other surface finishes may be produced by chemical or electrochemical treatment when high accuracy and reproducibility are required for fundamental corrosion studies.

The specimens should be degreased and cleaned, first with water and then with a suitable hot or cold solvent. The dried specimen should be measured and weighed to ± 0.1 or ± 0.5 mg, depending on its size. The cleaned specimens should not be touched with the fingers to avoid any effect of sweat, particularly when the specimen is to be exposed to a vapor or gas.

Exposure Equipment and Conditions

The equipment used for exposure of the specimens to the corrodent and the test conditions themselves differ with the purposes of the test and is designed to simulate the operating conditions as they are affected by variations in such factors as concentration of major and minor constituents and impurities, pH, temperature, velocity of fluids, and aeration. Some typical assemblies for exposing corrosion test specimens are shown in Figure 5.

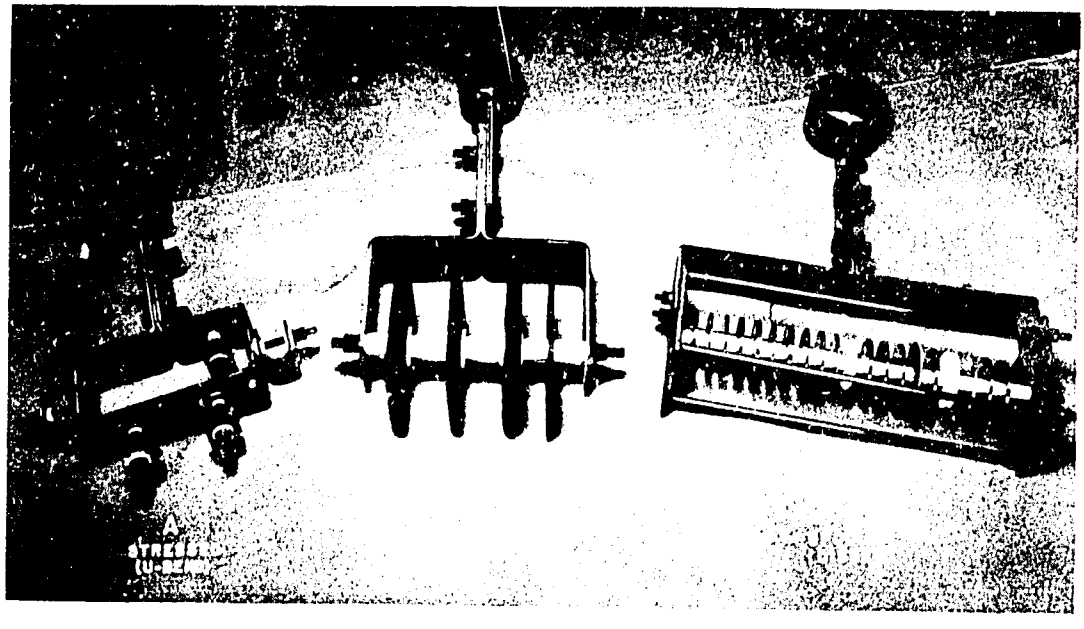


Figure 5. Typical Assemblies of Corrosion Test Specimens.

The specimens may be totally or partially immersed or exposed to the vapor phase above a liquid phase; they may be suspended or supported in specially designed test racks or arrangements (Appendices E and G).

The composition of the corrosive liquid or vapor should be controlled during the test, and its amount should be kept adequate. At the end of the test, it is useful to determine the extent of change in composition resulting from consumption of corrosive species, dissolution of corrosion products, and loss of liquid by evaporation. In some tests, the test solution should be replenished or replaced periodically.

The duration of the tests and the number of periods of exposure required depend on the type and rate of corrosion and on the reproducibility of the measurements. Each test should be made

for at least 3 periods of 48 hours each, with each period starting with fresh solution. The lower the corrosion rate is, the longer the test should be run.

A procedure for evaluating the effect of time in laboratory tests, called the "Planned Interval Test," is described in NACE standard TM-01-69.

On removal of the specimens from the corrodent at the end of the tests, their appearance should be observed and recorded before cleaning. The cleaning procedures required depend on the type of metal, the kind of corrosion, and the corrosion products or scale that are formed on the surface of the specimens.

Cleaning methods fall into three general classes, mechanical, chemical, and electrochemical, that are illustrated in NACE standard TM-01-69. The cleaning procedure should remove all the corrosion products with minimum removal of sound metal. As a general rule, brushing with a plastic brush under a stream of tap water or scrubbing with a spatula to remove scale are the easiest cleaning procedures.

Specimens may be cleaned before and after tests by ultrasonic techniques. The specimen is immersed in a suitable solvent (water, alcohol, or hydrocarbon) which is then radiated with ultrasound of sufficient energy to remove adherent solid particles. The shock waves hit the specimen surface in contact with the solvent and have a highly effective scouring action.

Evaluation of Results

The cleaned and dried corroded test specimens are weighed to determine the weight loss. They should then be examined with the naked eye, with a magnifying glass, and with a binocular microscope, and the type of corrosion, whether uniform or localized, should be identified.

Localized corrosion, such as pitting, crevice corrosion, intergranular attack, stress-corrosion cracking, or erosion corrosion, should be evaluated by special techniques given in papers dealing with the particular type of corrosion.[3]

Uniform corrosion may be expressed as loss in weight per unit of exposed area per unit of time of exposure, usually in units of milligrams per square decimeter per days, $mg/(dm^2)(day)$, and abbreviated as mdd.

---

3. A method for the assessment of pitting corrosion is illustrated in F. A. Champion. 1965. Corrosion Testing Procedures, 2d ed., John Wiley, New York, p. 205.

The weight loss may be converted into terms of the penetration or the loss of thickness of the metal. This expresses the loss in wall thickness of a metal vessel and is a measure of the expected life of the vessel under the test conditions. This conversion requires use of the density of the metal and is expressed as:

$$B = w/SD$$

where

B = penetration, or loss of thickness, cm

W = weight loss, g

S = exposed area of specimen, cm^2

D = density of metal, g/cm^3

To convert mdd to loss of wall thickness of a steel specimen in units of mils per year (mpy), a factor is derived by converting centimeters to mils (thousands of an inch), time from days to years, and taking the density of steel as 7.85 g/cm^3, whereby:

$$mdd/200 = mpy.$$

To convert mpy to millimeters per year (mmpy), divide mpy by 40.

$$mpy/40 = mmpy$$

The expression "mpy" is used in the United States, and the expression "mmpy" is used in some European countries. Additional expressions for corrosion rates, conversion factors, and densities of common metals and alloys are given in Appendix I.

Metals for handling chemical media are classified into three groups according to their corrosion rates:[4]

1. <5 mpy (< 0.13 mmpy)
   Metals in this group have good corrosion resistance and are suitable for valve seats, pump shafts, impellers, etc.
2. 5-50 mpy (0.13-1.3 mpy)
   Metals in this group are satisfactory if a higher corrosion rate can be tolerated, as in tanks, piping, and valve bodies.
3. >50 mpy (> 1.3 mmpy)
   Metals in this group usually are not satisfactory.

All important information and data obtained in corrosion tests should be reported. A form for presenting results of corrosion tests is given in Appendix J. Recommendations for reporting appear in standards NACE TM-01-69 and ASTM G31-72.

---

4. Uhlig, H. H. 1971. Corrosion and Corrosion Control (2d ed.), John Wiley, New York, p. 8.

CHAPTER 6

Electrochemical Techniques

Corrosion testing by weight-loss techniques is based on measurement of a weighed specimen during a specified time. The corrosion rate so determined is an average over a relatively short time, and it implies that corrosion proceeded uniformly over the whole surface and during the whole exposure time, an implication that may not be true.

It is common practice to express this gravimetric corrosion rate in $mg/(dm^2)(day)$ or in mils penetration per year to indicate loss of wall thickness without allowing for changes in corrosion rate with time or nonuniform corrosion.

Stability and strength are two of the basic properties of an engineering material that determine the suitability for its industrial use. Stability is the resistance to reaction with chemical and physical agents of its environment, and strength is the ability to withstand mechanical forces. In spite of their disadvantages, the gravimetric corrosion tests measure the loss of mass of the metal and hence the change in wall thickness of the equipment. These changes indicate the suitability of the metal, and the use of the tests is widespread. An additional factor is that these gravimetric techniques are simple and rapid.

Since corrosion is fundamentally an electrochemical process, as pointed out in Chapter 1, it is logical to apply electrochemical instruments and techniques to study corrosion phenomena. Measurements of changes in the electrical properties of the metal-environment system such as potential and current under carefully controlled conditions can yield information on instantaneous corrosion rates; passivity and passive films; and tendency to localized corrosion such as pitting, crevice corrosion, intergranular corrosion, and stress-corrosion cracking.

Electrochemical methods are applied extensively in basic investigations of the mechanism of corrosion, in corrosion testing, and in corrosion control in the chemical process industry. Instruments for electrochemical corrosion studies may be as simple as an electrochemical cell or as sophisticated as a potentiostat that automatically produces and records a polarization curve.

The application of several techniques and instruments will be discussed in this chapter, but the emphasis will be on the use of instruments available at IFDC.

Potential Measurements

In evaluating the corrosion process, measurement of the potential of the corroding metal is useful for predicting corrosion behavior, determining the tendency towards galvanic corrosion, following the development of passivity or its breakdown, and studying the effects of inhibitors and oxidizers and changes in properties of the solution and imposed conditions of temperature and agitation.

The electrode potential of an alloy depends on its chemical composition and metallurgical condition. The metallic specimen is immersed in a test solution, and its potential is measured against a reference electrode as described in the section "Potential, Current, and Resistivity." The electrode potential becomes stable on immersion for 30-60 minutes.

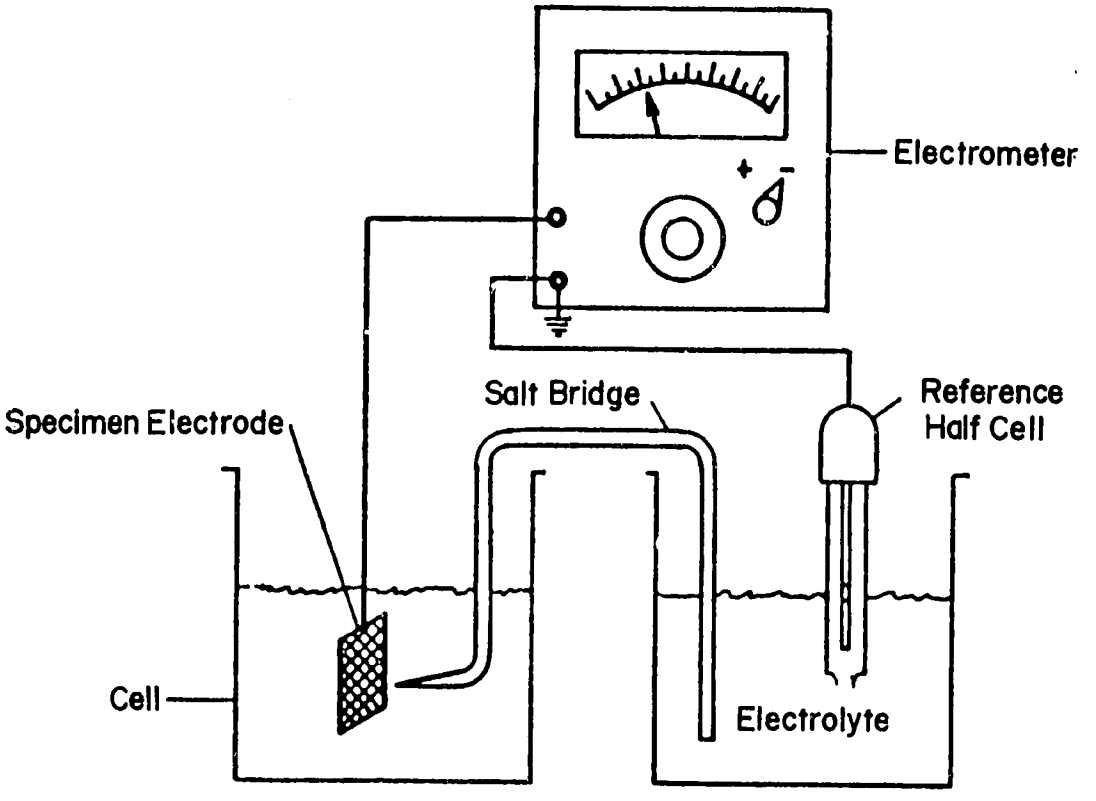
The half cell and potentials of common reference electrodes at 25°C are listed below:

Standard Electrode		Potential, volts
Hydrogen (SHE)	$Pt/H_2(a = 1)/H^+(a = 1)$	0.000
Calomel (SCE)	Hg/Hg_2Cl_2/Satd. KCl	+0.241
Silver-silver chloride	Ag/AgCl/1M KCl	+0.235

To illustrate the conversion of a potential measured with the standard calomel electrode to that of a potential against the standard hydrogen electrode, an electrode potential of 1.000 volt versus SCE would be 1.000 + 0.241 = +1.241 volt versus SHE, and an electrode potential of -1.000 volt versus SCE would be -1.000 + 0.241 = -0.759 volt versus SHE.

The potential of a metal is measured with a potentiometer or an electronic voltmeter in a setup such as that shown in Figure 6. In these setups the current flowing in the circuit is very small or near zero to avoid polarization of the electrode during the measurement. The prime requirement of a potential-measuring circuit is high impedance, and a pH meter with a suitable voltage scale or digital display panel is well suited for potential determination.

Variation of potential with time is recorded to study passive film breakdown and repair as indicated by decrease and increase in the potential, respectively, and to investigate the appearance and propagation of cracks resulting from stress corrosion of austenitic stainless steels in boiling saturated $MgCl_2$ solutions.



Note: The electrode potential of specimen is negative as shown.

Figure 6. Schematic Diagram of an Apparatus to Measure Electrode Potential of a Specimen. (Source: ASTM Standard G3-74).

Monitoring potentials during a corrosion process often is informative. For instance, failure due to stress corrosion cracking is accompanied by a distinct potential jump. The transition from the passive to the active state of stainless steel in acidic solutions or slurries is indicated by a sharp break in the plot of potential against time.

The redox potential of a solution (see the section on "Potential, Current, and Resistivity") can be measured by means of an electron-sensitive electrode, such as a bright platinum electrode combined with a standard calomel reference electrode. Measurements of strongly reducing solutions, such as those containing H_2S, must be made in a closed vessel, from which air is excluded.

Current-Potential Relationship

Since corrosion is an electrochemical process in which current and potential are the fundamental parameters, determination of the

current-potential relationship under carefully controlled conditions can yield information on the mechanism and rate of the corrosion process.

To study the corrosion behavior of a metal by means of polarization curves (see section "Polarization, Passivity, and Passivation), the anodic and cathodic reactions are measured separately on different specimens. A schematic in Figure 7. This arrangement comprises a polarization cell containing a three-electrode system--a specimen of the metal being tested (the working electrode), an auxilary electrode, and a reference electrode--immersed in the corrosive solution. A potentiostat applies and maintains a potential on the working electrode versus the reference electrode and measures the current between the working electrode and the auxiliary electrode. The potentiostat-electrometer combination provides the high impedance required for potential measurements.

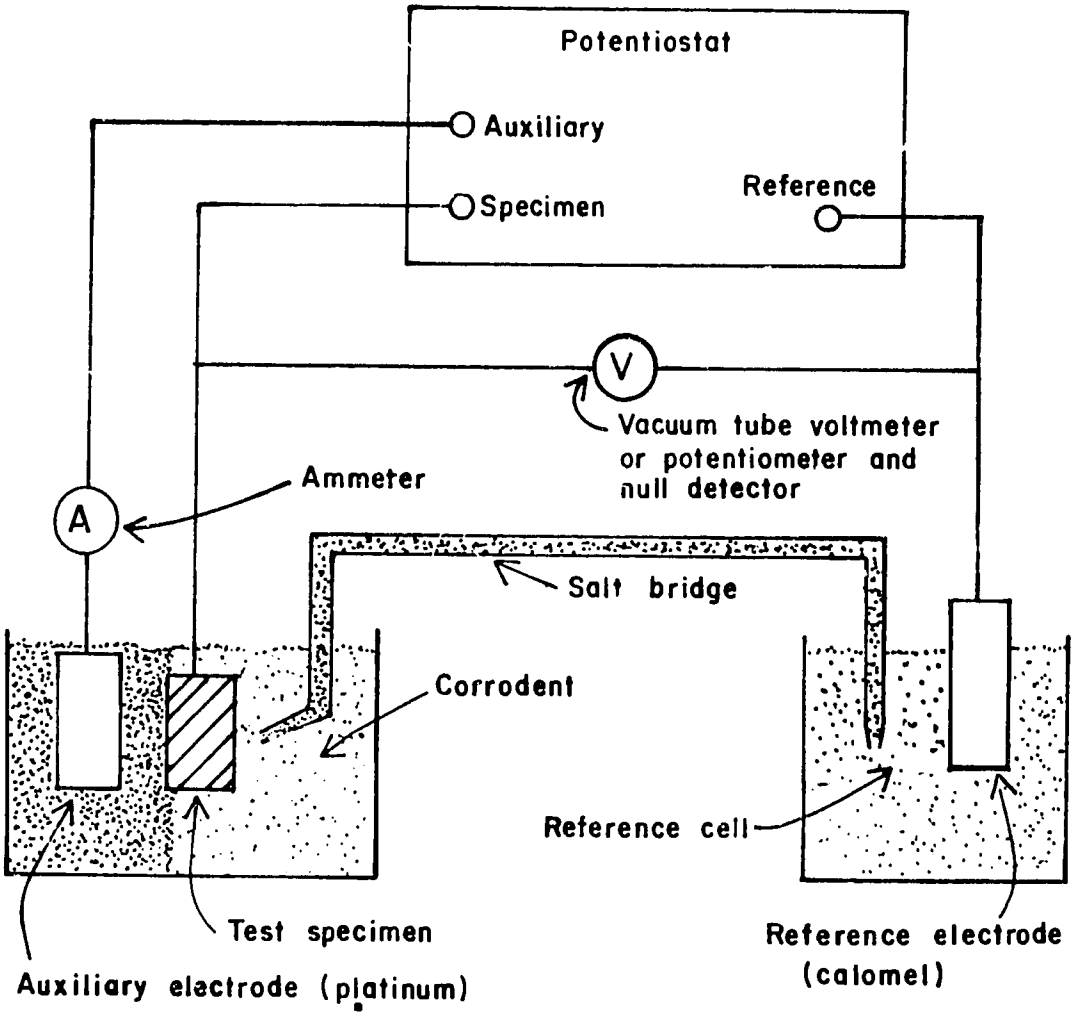


Figure 7. Schematic Diagram of a System to Measure Current-Potential Relationship.

Modern potentiostats contain electronic devices for continuous automatic scanning of the potential, logarithmic converters, and X-Y recorders for reproducing potentiodynamic and potentiostatic polarization curves.

If the potential is plotted against the current on a semilogarithmic paper (in accordance with ASTM standards G3-74 and G5-72), current density-potential diagrams, such as those shown in Figures 8 and 9, are obtained. Conventions for signs of potential and current density and for graphic presentation of data are given in ASTM standard G3-74.

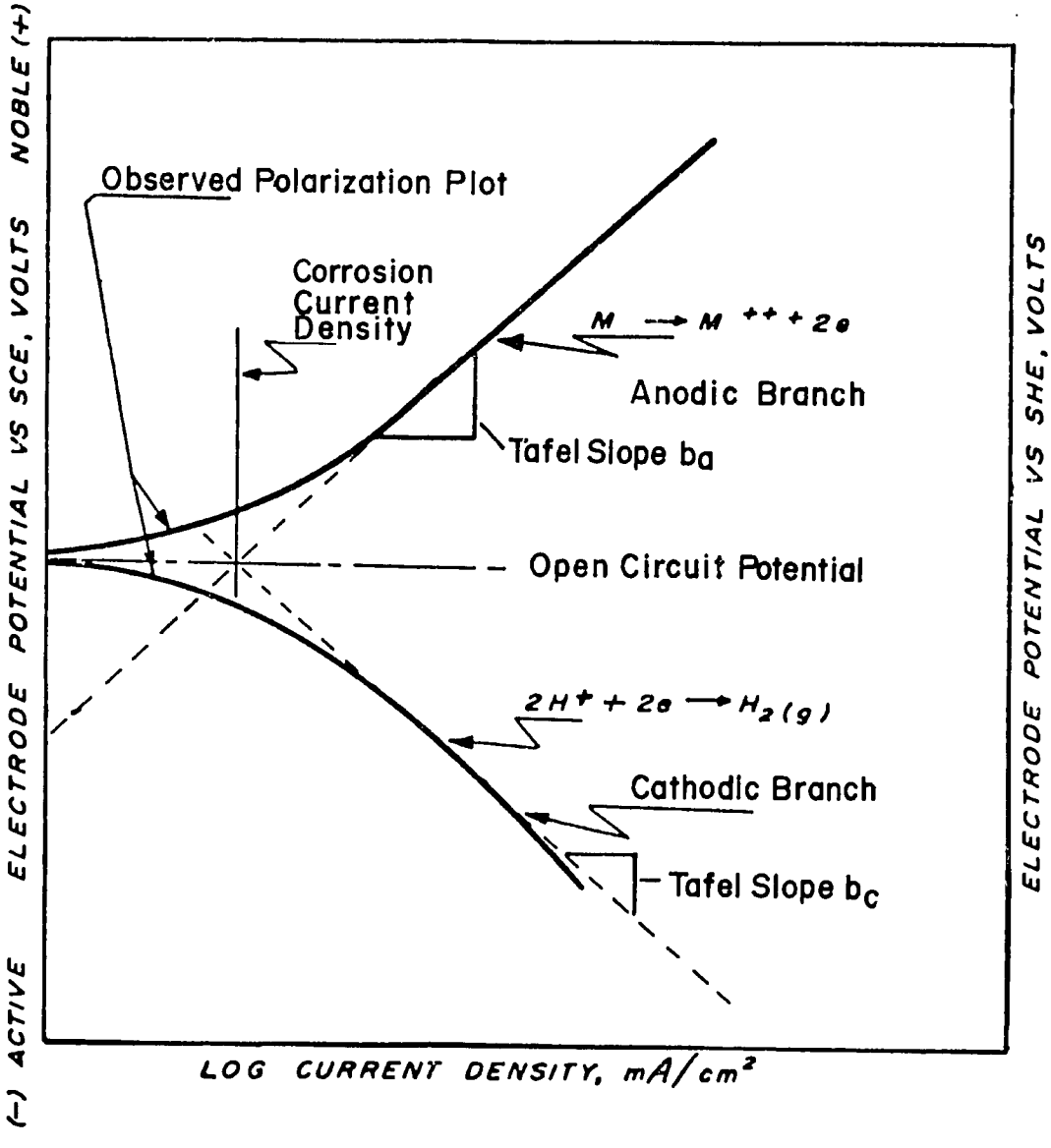


Figure 8. Hypothetical Cathodic and Anodic Polarization Diagram. (Source: ASTM Standard G3-74).

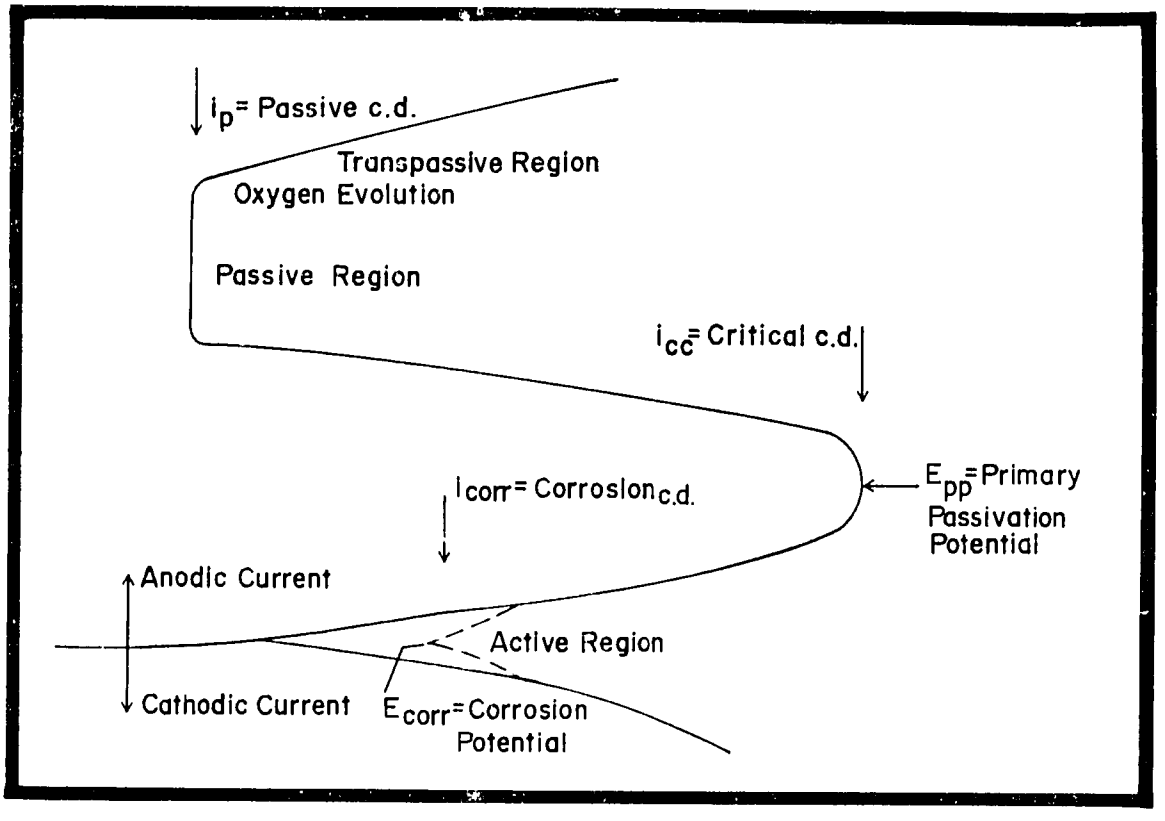


Figure 9. Hypothetical Cathodic and Anodic Polarization Plots for a Passive Anode. (Source: ASTM Standard G3-74).

Figure 8 shows typical anodic and cathodic polarization curves for an active metal-solution combination. The curves are nonlinear at low currents but become linear at a higher current. This linear part of the plot is called the Tafel region, and it is characterized by the Tafel anodic (b_a) and cathodic (b_c) slopes.

The anodic and cathodic plots are described by the Tafel equation:

$$\eta = a + b \log i$$

where:

η = overvoltage, the difference between the potential of the specimen and the corrosion potential

a = a graphical constant of the plot

b = Tafel slope

i = current density at overvoltage η

This equation gives a straight line with slope b when η is plotted versus log i.

Figure 9 contains typical anodic and cathodic polarization plots for a passive metal-solution combination that traverses three regions of corrosion behavior--active, passive, and transpassive (see section "Polarization, Passivity, and Passivation). The electrochemical parameters of the corrosion behavior such as the critical current density i_{cc} and the passivation potential E_{pp} are located.

Polarization curves are used for determination of corrosion rates according to the following methods:

1. Extrapolation of both Tafel slopes to intersect at the corrosion density, i_{corr} (Figures 8 and 9).
2. Extrapolation of the cathodic Tafel slope to intersect with the corrosion potential (Figure 8).
3. Linear polarization (Figure 10) based on the Stern-Geary equation:

$$\frac{\Delta E}{\Delta i} = \frac{b_a b_c}{2.3(b_a + b_c)i_{corr}}$$

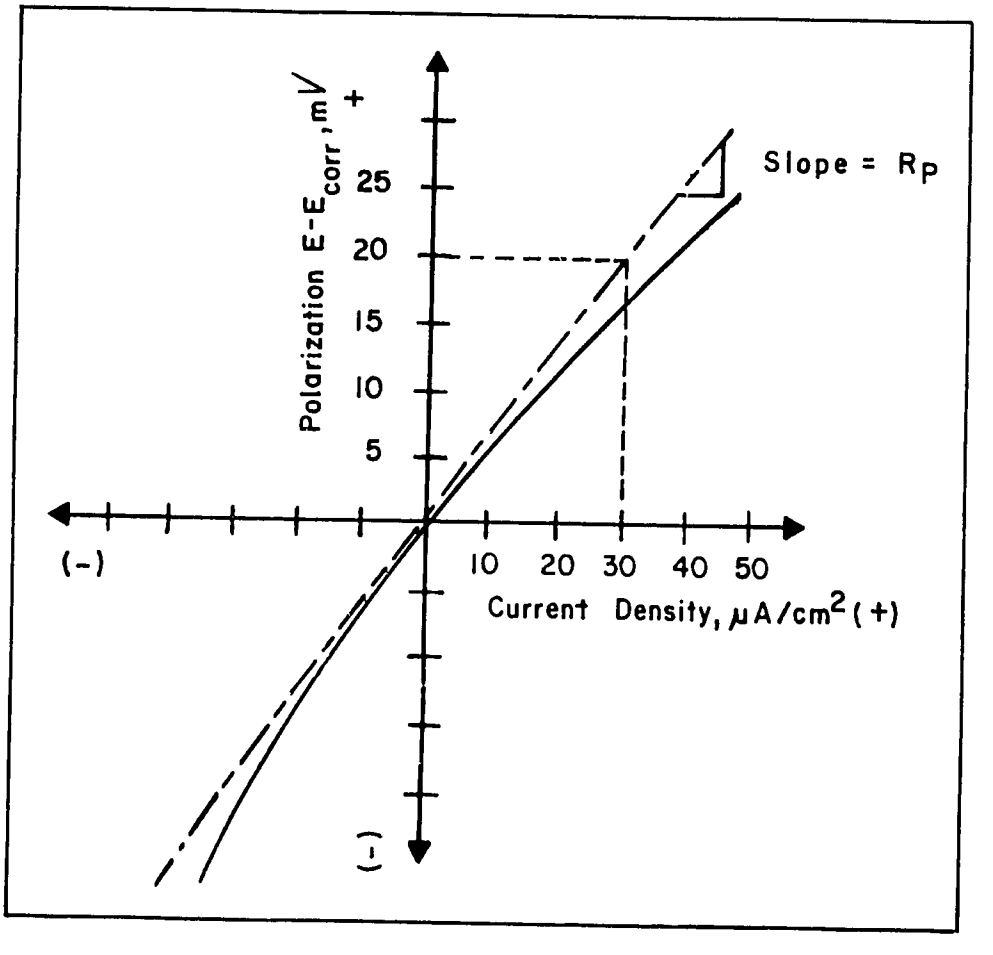


Figure 10. Hypothetical Linear Polarization Plot. (Source: ASTM Standard G3-74).

that relates the corrosion current density, i_{corr}, to the slope of the linear polarization plot, R_p or $\Delta E/\Delta i$, and

where:

b_a = anodic Tafel slope

b_c = cathodic Tafel slope

ΔE = the difference $E-E_{corr}$, where E is the specimen potential and E_{corr} is the corrosion potential

Δi = the change in current density required to produce a ΔE of 10-20 mV

The linear polarization technique is based on the fact that within about 10-20 mV of the corrosion potential the overvoltage varies linearly with applied current.

Assuming that anodic and cathodic Tafel slopes with values of 120 mV represent the average of all corrosion systems, the Stern-Geary equation reduces to:

$$\frac{\Delta E}{\Delta i} = \frac{26 \text{ mV}}{i_{corr} \ \mu A/cm^2}$$

and

$$i_{corr} = \frac{26}{\Delta E/\Delta i} \ \mu A/cm^2$$

An example of the determination of i_{corr} from the linear polarization curve in Figure 10 is shown below.

$$\text{slope} = \frac{\Delta E}{\Delta i} = \frac{20}{30} = 0.66 \text{ mV}/(\mu A/cm^2)$$

$$i_{corr} = \frac{26}{\Delta E/\Delta i} = \frac{26}{0.66} = 39 \ \mu A/cm^2$$

which is roughly equivalent to 100.0 mdd or 20.0 mpy or 0.5 mmpy.

A summary of the electrochemical parameters obtained from polarization plots is given in Appendix J, which may be used for reporting results from electrochemical measurements.

Galvanostatic (constant current), potentiodynamic (automatic potential sweep), and potentiostatic (constant potential) polarization techniques are of value in predicting corrosion behavior and in designing corrosion control devices. They have been applied in studies of passivity, pitting, and stress-corrosion cracking, in development of corrosion-resistant alloys for chemical process industry, in selection of corrosion inhibitors for industrial cooling water, in the development and application of anodic protection systems, and in the investigation of the behavior of metals in molten salts.

Measurement of Corrosion Factors

The composition of an electrolyte solution and its properties have a major influence on the corrosion process, its magnitude, and the type of corrosion. The main factors that affect the electrochemical parameters of corrosion and are normally measured by electrochemical techniques are pH, dissolved oxygen, and electrolytic conductivity.

pH Measurement--pH is a measure of the acidity or alkalinity of an aqueous solution. Acids owe their acidity to the hydrogen ion (H^+); this acidity is expressed by the hydrogen ion concentration. The electrometric pH measurement is based on the fact that, when immersed in a solution, certain electrodes develop voltages that depend on the H^+ concentration of the solution.

The glass electrode is the most useful electrode for determination of the pH of a solution; this electrode is immersed in the solution along with a reference calomel electrode. The potential of the glass electrode varies with the activity of the hydrogen ions and can be read on an electronic voltmeter scale. Modern pH meters are fully transistorized, have a high input impedance, and automatically present the results on a digital display panel.

The pH measurements in fertilizer solutions or soils are useful in predicting the corrosion characteristics of the environment or the anticipated corrosion of metals such as iron and aluminum and their alloys. To obtain comparative pH values, measurements should be made on fertilizer solutions with the same molar or percentage concentrations.

Dissolved Oxygen Measurement--Most aqueous solutions, from natural waters to industrial waters to fertilizer solutions, are in contact with the atmosphere and contain dissolved oxygen. The dissolved oxygen content of pure water at 20°C is about 10 ppm, but it decreases with increase in temperature and with increase in dissolved salt concentration. For example, concentrated brines containing 20% salt may contain not more than 1-2 ppm dissolved

oxygen. It is important to know the oxygen content of aqueous solutions because corrosion depends on the diffusion of oxygen from the bulk of the solution to the metal surface and its subsequent cathodic reduction (see section "The Electrochemical Nature of Corrosion").

The determination of oxygen in water is based on the electrochemical reduction of oxygen at its reduction potential. This reduction produces an electrical current, and this current is proportional to the amount of oxygen present.

Several commercial instruments for this determination are available, most of them consisting of a direct reading meter and a polarographic sensor or an oxygen electrode to be immersed in the solution. The electrode assembly consists of an electrolytic cell comprising a cathode, an anode, and an electrolyte mounted in a plastic housing with a membrane that is permeable to oxygen but impermeable to water and interfering ions.

Electrode oxygen meters are used in laboratory corrosion research and in the chemical industry for monitoring corrosion in water-handling systems, in sweet and sour brines in the oil industry, in water sewage and plant effluents, and in food and beverages.

Electrolytic Conductivity Measurement--Electrolytic conductivity is the measure of the ability of the ions of a solution to carry an electrical current. It is expressed by a value called the specific conductance (see section "Potential, Current, and Resistivity").

Conductivity is usually measured by determination of the resistance of the solution by an ac Wheatstone Bridge. A typical instrument consists of an ac Wheatstone Bridge circuit, a conductivity cell, and a null indicator.

Corrosion phenomena such as galvanic corrosion and pitting are accelerated in solutions with high conductivity, such as liquid fertilizers and brines. In conductivity determinations made to elucidate the mechanism of pitting corrosion of stainless steel, it was necessary to measure the conductivity of the solution in the vicinity of the corroding surface, which is not the same as that in the bulk solution because of the presence of soluble corrosion products. Measurements of potential, conductivity, pH, and Cl^- concentration are made adjacent to the metal surface and at the bottom of the pits through use of micro-manipulators and capillaries as probes.

Conductometers are used for determinations of electrolytic conductivity in chemical process liquors, of soil moisture content, of fertilizer content of greenhouse soils, and of concentration of brines in foods, and for monitoring water treatment. Information on the conductivity characteristics of soil, water, or chemical systems is necessary for the calculation of the required current output of protective anodes and for the design of cathodic protection equipment operating in these environments. Conductivity values provide an indication of the corrosiveness of certain environments; in general, the higher the conductivity the more corrosive the environment.

Corrosion Measuring Instruments

A number of commercial instruments that are based on electrochemical principles are used to determine the corrosion behavior of metals in electrolyte solutions. These instruments consist of a probe containing the metal or alloy to be tested and an electronic meter that measures corrosion as it occurs in the plant or the laboratory. Several commercial instruments based on either of two methods--electrical resistance or linear polarization resistance--including those used in the IFDC laboratories are described below.

Electrical Resistance Method--The Corrosometer measures the corrosion rate of a metal probe with different geometric forms, such as wire, tube, or strip, by periodically measuring its increasing resistance as the probe diameter decreases because of corrosion.[5] The accuracy and reliability of the instrument depend on the temperature and velocity of the liquid.

The instrument reading is converted to a metal loss, equivalent to the corrosion rate, in mils per year. Measurements in the fertilizer industry can be made by locating the instrument in pipes or vessels. The probes can also be inserted in gaseous or mixed phase systems to estimate the corrosive effect of plant off-gases or air pollutants.

Linear Polarization Resistance Instruments--These instruments are based on the linear polarization method, previously described in section "Current Potential Relationship." Two types of instruments are available for measuring corrosion rate by this method, one employing a two-electrode probe and the other a three-electrode probe.[6] When the probe is immersed in the corrosive

5. Corrosometer Model CK2, manufactured by Magna Corporation, U.S.A.
6. Three-electrode Petrolite Corrosion Rate Meter, manufactured by Petrolite Instruments, U.S.A., and two-electrode Corrater, manufactured by Magna Corporation, U.S.A.

solutions, the instrument applies a potential of 10-20 mV on the test electrode versus the reference electrode to polarize the test electrode. The current flowing then is proportional to the instantaneous corrosion rate, and by a suitable calibration the corrosion current is converted to units of mils per year, expressing the loss of wall thickness.

The instruments provide an estimation of pitting tendency as indicated by the difference between the two measurements when the current flow is reversed.

The Petrolite Corrosion Rate Meter--This instrument can be used to measure corrosion rates in solutions with a wide range of specific conductance, such as fertilizer intermediates and products and liquid fertilizers. The test electrodes are detachable from the threaded probe studs and can be used also for measuring weight loss in a separate test, and the corrosion rates obtained may be compared with those determined by the instrument.

The Potentiostats--The operating principles of the potentiostat and its wiring diagram are described in section "Current Potential Relationship" and illustrated in Figure 7. Potentiostats and instrumentation systems for performing and recording corrosion behavior diagrams are readily available with several models produced commercially under their own trade names.[7]

The application of the potentiostat has been growing steadily and has contributed greatly to the knowledge of corrosion processes and passivity because it is particularly suitable for accelerated corrosion tests.

The Potentiodyne Analyzer--This instrument (Figure 11) records potentiodynamic and potentiostatic measurements in a corrosion cell. The corrosion cell contains three electrodes--a test electrode, an auxiliary electrode, both made of the same alloy being tested, and a reference silver electrode.

In the potentiodynamic mode the instrument measures a polarization current in the cell resulting from a cell voltage that sweeps between two limits. In the potentiostatic mode the instrument measures polarization currents at selected values of constant voltage.

---

7. The Potentiodyne Analyzer, Petrolite Instruments, U.S.A.; Anotrol Research Potentiostat, Magna Corporation, U.S.A.; Corrosion Measurement System Model 350, EG & G Princeton Applied Research, U.S.A.; Potentiostat Alpha Research Co., U.S.A.; DOS Analyzer ECO, U.S.A.; Wenking Potentiostat, Gerhard Bank Elektronic, West Germany; Corroscript, Tacussel Electronique, France.

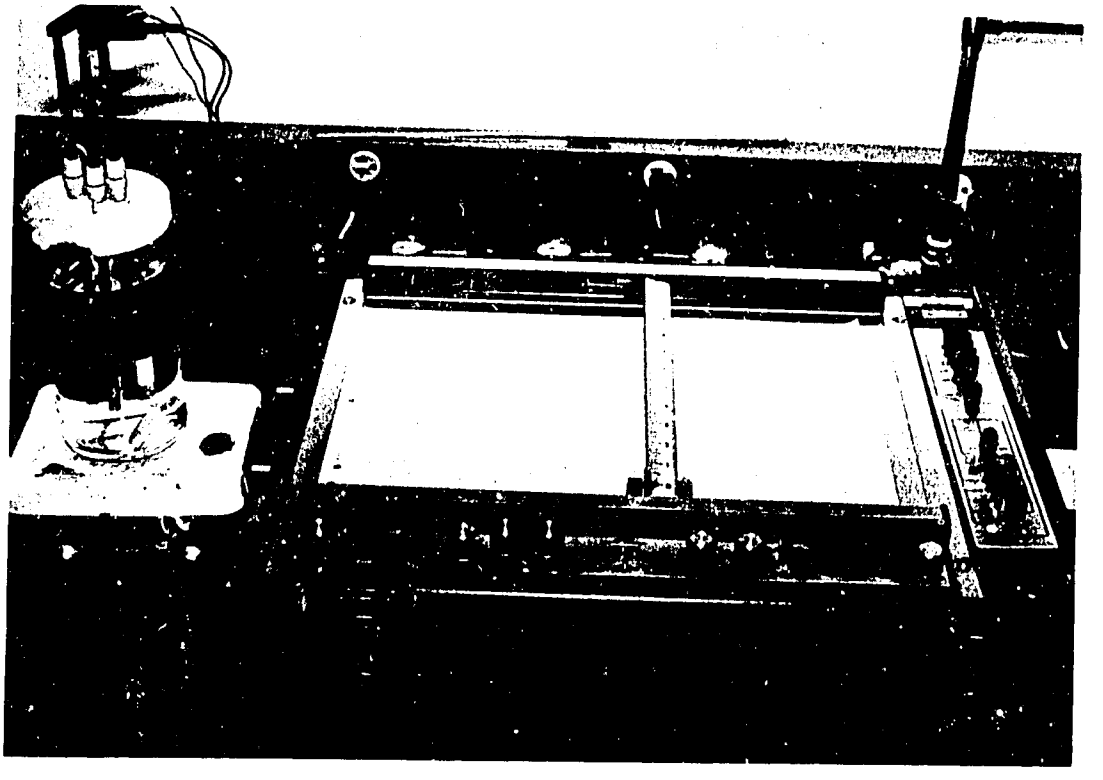


Figure 11. Potentiodyne Analyzer Used by IFDC for Corrosion Measurements.

The instrument can be used also as a potentiometer for recording the change with time of the potential of a metal immersed in an electrolytic solution and for measuring galvanic currents over periods of time. The data obtained are useful for assessing the corrosion behavior of a metal in a test solution.

The polarization curves automatically recorded by the Potentiodyne Analyzer are used for determination of corrosion behavior and for determination of corrosion rates, as explained in the section "Current Potential Relationship."

The Potentiodyne Analyzer performs in the plant as well as in the laboratory. The instrument may be used for:

1. Selection of corrosion inhibitors in cooling water systems;

2. Determination of corrosion characteristics of fertilizer;

3. Determination of effects on corrosion rates of impurities in fertilizer intermediates and products such as Cl^- and F^- in phosphoric acid (see Figure 12);

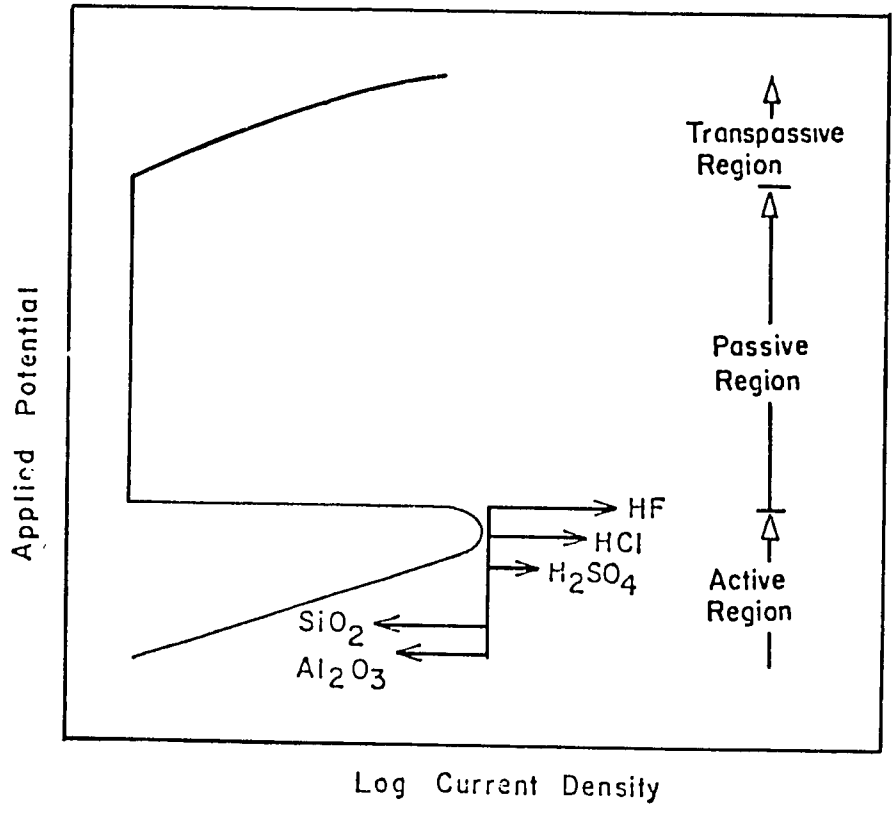


Figure 12. Anodic Polarization Curve Showing the Effect of Impurities on Stainless Steel Corrosion in Phosphoric Acid.

4. Determination of the influence of oxidizing agents, such as Fe^{+3}, NO_3^-, and $CrO_4^=$;

5. Determination of the influence of erosive conditions on the corrosion behavior of stainless steels;

6. Studies of passivity and passivation;

7. Development of anodic protection systems for chemical plant equipment;

8. Corrosion studies in pilot plants;

9. Selection of materials of construction for fabrication of chemical equipment; and

10. Investigation of corrosion failures in chemical plants.

CHAPTER 7

Corrosion in Wet-Process Phosphoric Acid (WPA)

Two main processes are used to produce phosphoric acid: the wet process (WPA), based on attack of phosphate rock by sulfuric acid, and the thermal process in which the phosphate rock is reduced to elemental phosphorus which is oxidized and hydrated to phosphoric acid. In other wet processes, phosphate rock is acidulated with hydrochloric or nitric acid. The composition and purity of the phosphoric acid obtained by these processes depend upon the composition of the phosphate rock and the acid used. Chemical compositions of phosphate rocks are listed in Appendix K.

The wet process consists of three main stages:

1. Acidulation of phosphate rock by sulfuric acid.

2. Filtration to separate the solids, mainly gypsum, from the filter acid, 30% P_2O_5.

3. Concentration by evaporation of the filter acid to merchant-grade acid, 52%-54% P_2O_5.

To understand the corrosion mechanisms in WPA manufacture, it is necessary to know the chemical reactions that occur during the acidulation and concentration stages. The overall reaction between fluorapatite and sulfuric acid is usually expressed as:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 = 10CaSO_4 + 6H_3PO_4 + 2HF$$

The hydrogen fluoride may react with any active silica present to form silicon tetrafluoride:

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$

which may volatilize as such or hydrolyze to fluosilicic acid:

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$$

The fluorine then may form insoluble compounds such as Na_2SiF_6 and K_2SiF_6 that precipitate from the system. The fluorine compounds undergo further reactions which will be dealt with in the section "Influence of Impurities."

The sulfuric acid reacts with any calcium carbonate and heavy metal oxides present in most rock:

$$CaCO_3 + H_2SO_4 = CaSO_4 + CO_2 + H_2O$$

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O$$

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$$

Phosphate rocks containing chlorides, such as NaCl, yield hydrochloric acid:

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$$

During the attack and concentration stages, fluorine and chlorine are evolved as vapors of SiF_4, HF, and HCl, lowering the content of F^- and Cl^- in the filter and concentrated phosphoric acids.

Because of the corrosive conditions encountered in the production of WPA, particularly in the reaction section, corrosion-resistant materials of construction are required for the plant's chemical equipment. These materials include plastics and elastomers, stainless steels from the AISI 300 series, high-alloyed stainless steels, and Ni-base alloys. In spite of the wide use of these alloys, however, corrosion and erosion failures are often reported especially of equipment subjected to severe hydrodynamic conditions such as pumps and their impellers that are made of base metal or lined with rubber. Figure 13 shows typical corrosion encountered by a pump impeller used for pumping wet-process phosphoric acid.

References on corrosion problems in WPA plants, corrosion tests in WPA, and selection of materials for WPA plants are given in the bibliography. A list of materials of construction and linings used in the phosphoric acid industry is presented in Appendix L.

Figure 13. Typical Corrosion of Durimet 20 Pump Impeller in As-Cast Condition After Exposure to Nominal 54% H_3PO_4 Wet-Process Phosphoric Acid.

Austenitic stainless steels are resistant to corrosion by solutions of pure phosphoric acid because of the stability of the passive oxide film, but in the production of WPA this protective layer may be destroyed by corrosive impurities, severe operating conditions, or a synergistic action of the two that results in markedly increased corrosion rates.

Influence of Impurities

Phosphate rock is the principal source of dissolved and suspended impurities in WPA.[8,9] Other impurities such as Cl^- may be introduced in process water, particularly brackish water. Sometimes contaminated sulfuric acid obtained from the hydrometallurgy industry introduces additional impurities. The impurities impart undesired color and turbidity to the WPA and increase the corrosiveness of the acid. Cl^- and F^- are particularly corrosive, and other impurities that affect corrosion are SiO_2, Al_2O_3, alkali metal salts, $SO_4^=$, $S^=$, organic matter, and oxidizing agents. The corrosivity of a specific impurity depends on its chemical nature, the concentration of its active species, and its interaction with other acid constituents and with the surface of the specific metal. The amounts of several impurities supplied by phosphate rock and found in filter acid and concentrated acid are shown in Table 3.

Table 3. Impurities in Phosphate Rock and Wet-Process Phosphoric Acid[a]

Impurity	Impurity Range Level in Phosphate Rock, %	Filter Acid	Concentrated Acid
		%	
H_2SO_4	0.15-4	1-4	1-4
F^-	2-4	0.2-3.5	0.1-1.5
Cl^-	0.02-1.0	0.005-0.1	0.002-0.05
SiO_2	0.5-4	0.05-1.8	0.01-0.7
Al_2O_3	0.2-3	0.2-3	0.2-3
Fe_2O_3	0.2-3.5	0.2-3	0.1-2.5
MgO	0.1-1.8	0.1-1.5	0.1-1.5

a. Source: Bernhardson, S. O., and R. Osterholm. 1978. Information Chimie, No. 176, p. 125.

In addition to affecting corrosion, some impurities change the density and viscosity of the acid and form acid sludges and sediments. In contact with metallic surfaces these sediments may influence the corrosion behavior of the metal by forming deposits that promote localized corrosion.

8. Lehr, J. R. 1968. "Nature of Impurities," In Phosphoric Acid, A. V. Slack, ed., p. 637-684, Marcel Dekker, New York, New York.
9. Hein, L. B. 1968. "Removal of Impurities," In Phosphoric Acid, A. V. Slack, ed., p. 687-708, Marcel Dekker, New York, New York.

Effect of Chloride Ion--The chloride ion in phosphoric acid comes from phosphate ores in which it is present as an alkali metal chloride, such as NaCl. It may be removed by washing with fresh water, but it may also come from the wash water since seawater is sometimes used for washing the phosphate rock or for rinsing tanks or cargo holds. The Cl^- content then can rise to a dangerous level. Chloride may also occur in the apatite itself, sometimes as a water insoluble salt or as an oxychloride formed during calcination of the phosphate rock.

Chloride contamination also may result from handling and storing of raw materials. In many fertilizer plants phosphate rock and muriate of potash (KCl) are unloaded with the same equipment and stored in bulk in the same building.

Small amounts of potash often are left in elevators and conveyors and may be mixed with the phosphate rock subsequently handled in the equipment.

The corrosivity of the halogen acids, HCl and HF, and of the halide ions Cl^- and F^- in strong mineral oxygen-acids, such as H_3PO_4 and H_2SO_4, is related to the physicochemical properties of the halogens, and their electronegativity, ion size, and ionic character of the HX molecule indicate their high chemical reactivity. Chloride ion is adsorbed on metal surfaces and replaces adsorbed oxygen or water molecules. This shifts the potential of the metal to more active (electronegative) values and causes breakdown of the passive state, mainly at elevated temperatures, which leads to the formation of pits. During attack on stainless steel, chlorides of iron, nickel, and chromium are formed: these are highly soluble in phosphoric acid because of its complexing of cations of the transition group elements.

The values of the electrochemical parameters of the anodic polarization curve, such as i_{cc} which indicates corrosion activity, increase with increasing Cl^- concentration.

Effect of Fluoride Ion--The CaF_2 constituent of the fluorapatite of phosphate rock reacts with sulfuric acid during acidulation to produce hydrofluoric acid which may form HF_2^- and F^- ions, depending on the hydrogen ion activity of the solution according to the equilibrium.

$$(HF)_2 \rightleftarrows 2HF \rightleftarrows HF_2^- + H^+ \rightleftarrows 2F^- + 2H^+$$

HF dimer	free HF	hydrofluoride ion	fluoride ion	hydrogen ion

HF reacts with any active silica in the rock:

$$6HF(aq) + SiO_2(s) \rightarrow H_2SiF_6(aq) + 2H_2O(1)$$

Some of this fluosilicic acid volatilizes as silicon tetrafluoride:

$$H_2SiF_6(aq) \rightarrow SiF_4(g) + 2HF(g)$$

but some of the SiF_4 may hydrolyze to form additional HF and deposits of hydrated silica:

$$SiF_4(g) + 2H_2O(1) \rightarrow 4HF(aq) + SiO_2(s)$$

Dissolved aluminum compounds form acid-soluble aluminum fluoride complexes, e.g., $(AlF_6)^{-3}$. (Formation of fluoride complexes and calculation of the complexing ratio $[Si + Al]/F_6$ are illustrated in Appendix M.) Other reactions that decrease corrosion include formation of partially soluble metal fluoride complexes with Fe^{+3}, Mg^{+2}, Ca^{+2}, and Na^{+}, and formation of insoluble fluoaluminates and fluosilicates that settle on metallic surfaces, such as Na_2SiF_6, $NaKSiF_6$, $MgNaAlF_6$, Na_3AlF_6, and $MgSiF_6$.

The main corrosion agent is the free fluoride ion, which is not complexed by cations. Reactive silica decreases the free HF by forming SiF_4 or H_2SiF_6. When the silica content of the rock is relatively less than the fluorine content, addition of reactive silica in the acidulation stage is recommended as a means of decreasing corrosion. This effect can be obtained also by mixing the rock with another phosphate rock that is high in reactive silica or aluminum compounds.

These effects have been demonstrated in laboratory corrosion tests with 30% P_2O_5 phosphoric acid to which HF or complex fluorine compounds such as H_2SiF_6 were added. The tests included weight loss and electrochemical techniques. The electrode potential of AISI-type 316 stainless steel becomes active in the presence of HF, indicating a tendency to corrosion, and the electrochemical parameters (see Appendix J) of the anodic polarization curve reveal anodic dissolution as a result of addition of HF and stable passive behavior in the presence of H_2SiF_6 (see Bibliography for relevant papers).

Effect of H_2SO_4--Sulfuric acid is a strong mineral acid with oxidizing properties. The corrosion resistance of carbon steel to sulfuric acid is based on the formation of a protective adherent

layer of $FeSO_4$, which is insoluble in the concentrated acid. On the other hand, stainless steels withstand cold dilute sulfuric acid because of the stability of their protective passive films.

WPA always contains some free sulfuric acid. The contribution to corrosion of this acid in filter acid and concentrated acid depends on two factors.

1. One is the ionic strength of the solution, particularly the activity of the hydrogen ion. Free sulfuric acid lowers the pH of phosphoric acid solutions and so may affect the passive film of stainless steels.

2. Increase in the sulfuric acid content promotes decomposition of the noncorrosive fluorosilicate and fluoroaluminate complexes and formation of free HF and so increases corrosion. In some plants, small amounts of phosphate rock are added after the main acidulation to lower the free sulfuric acid content.

Influence of H_2S--Some phosphate rocks contain as much as 1% sulfide sulfur (Appendix K). In acidulation the sulfide is converted to H_2S, a weak acid that dissociates as in the equilibrium:

$$H_2S \rightleftarrows H^+ + HS^- \rightleftarrows 2H^+ + S^=$$

H_2S and the sulfide ion may act as reducing agents that affect the stability of the passive film on metals. Results of tests in a laboratory acidulation to which H_2S was added showed that the potential of stainless steel 316 fell slowly until it became negative, corresponding to active corrosion of the metal.

Influence of Oxidizers--The oxidizing agents present or occasionally added to phosphoric acid fall into three groups:

1. Oxidizers contained in the phosphate rock or inherent in the operating conditions, such as Fe^{+3} resulting from dissolution of Fe_2O_3, or oxygen dissolved or supplied by aeration, mixing, agitation, or other operations that increase the exposure of the acid to air.

2. Metallic cations, such as Fe^{+3}, Cr^{+3}, or Cr^{+6}, Ni^{+2}, and Mo^{+6}, that are formed by corrosion of stainless steels or Ni-base alloys. These cations usually are present in low concentrations, but during severe corrosion at stagnant spots they may accumulate and accelerate corrosion.

3. Oxidizing agents, such as HNO_3 and cupric salts, that may be added to WPA to decrease the corrosion of stainless steel.

This procedure is not widely used because some oxidizing agents damage the rubber lining of the reactors. The behavior of oxidizing agents in WPA is complex and depends mainly on their interaction of the agents with the species present in the acid and with the metal. For example, ferric ions accelerate the corrosion of carbon steel in acids. They contribute an additional cathodic reaction, the reduction to ferrous ions, and in the bulk solution the ferrous ions may be reoxidized to ferric ions, thereby replenishing the supply of the deleterious oxidizing agent.

On the other hand, some oxidizers may be beneficial to stainless steels because they move the corrosion potential in the noble direction and thus into the passive region.

The oxidizing power of WPA is measured with an inert electrode, such as platinum, with reference to a standard calomel electrode (see section "Potential Measurements"). A summary of the effects of the impurities in WPA is given in Table 4, and their effects on the shape and the electrochemical parameters of the anodic polarization curve are presented in Figure 12.

Effect of Operating Conditions

WPA plants operate under severe conditions that include elevated temperatures and rapid heat transfer, high acid concentration, agitation and circulation of liquids containing erosive suspended solids, aeration, formation of foam, and volatilization of corrosive acidic vapor that condenses on cooler metallic surfaces. Destructive corrosion results from combinations of these factors in which their combined action is greater than the sum of their separate actions.

Effect of Acid Concentration--Phosphoric acid is a mineral nonoxidizing acid; its first dissociation follows the equilibrium:

$$\underset{(25^\circ C)}{} \quad H_3PO_4 \rightleftarrows H^+ + H_2PO_4^- \qquad K_a = 7.52 \times 10^{-3}$$

The corrosivity of pure phosphoric acid solutions increases with increase in concentration to about 60% H_3PO_4 and then decreases with further increase in concentration. This behavior parallels the hydrogen ion concentration which increases with increase in acid concentration to about 50% H_3PO_4 and then decreases as the equilibrium in concentrated acid shifts to the left with further increase in acid concentration. Sulfuric acid solutions behave similarly. In both phosphoric and sulfuric acids there is a fairly good correlation between hydrogen ion concentration and the rate of corrosion.

Table 4. Summary of Effects of Impurities on Corrosion in Wet-Process Phosphoric Acid[a]

Impurity	Effect on Corrosion Tendency	Effect on Anodic Polarization Curve	Formation of F^- Complexes	Contribution to the Cathodic Process	Net Effect on Corrosion
F^-	Strong increase	i_{cc} increases			Increase
Cl^-	Increase at elevated temperature	icc increases			Increase
H_2SO_4	Increase due to acid activity	Depends on the presence of F^- and Cl^-	Decomposition of F^- complexes		Increase
Si^{+4}	Decrease	Stable passivity	Yes		Decrease
Al^{+3}	Decrease	Stable passivity	Yes		Decrease
Fe^{+3} and other oxidizers	Depends on content and conditions	Depends on content and conditions	No	Yes, due to $Fe^{+3} + e \rightarrow Fe^{+2}$	Depends on content and conditions
H_2S	No firm data	No firm data			No firm data

a. Source: Bernardson, S. O., and R. Osterholm. 1978. Information Chemie, No. 176.

In the WPA process, 30% P_2O_5 acid is concentrated to 52%-54% P_2O_5 by vacuum evaporation with steam-heated heat exchangers. Typical compositions of filter and product acids from Florida phosphate rock are listed below.

	Composition, %					
	P_2O_5	CaO	F	H_2SO_4	Al_2O_3	Fe_2O_3
Filter acid	30.0	0.5	2.5	1.6	0.9	1.1
Product acid	54.0	0.0	1.2	2.9	1.5	2.0

The acid is very corrosive, particularly to heat-exchanger surfaces where temperatures and velocities are high. During the concentration, part of the salts, such as fluorine compounds, precipitate and either form scale on the surfaces of the evaporators or remain in suspension. Fluorides are evolved with the water vapor:

$$H_2SiF_6(aq) \xrightarrow{\text{heat and acid}} SiF_4(g) + 2HF(g)$$

and Cl^- ions are removed as HCl vapor.

The corrosivity of halide ions in pure 30% and 50% H_3PO_4 decreases in the order $F^- > Cl^- > Br^-$ in accordance with the chemical activity of the halides. In 70% and 85% H_3PO_4 (51% and 62% P_2O_5), however, the corrosivity of the halides is in the order $Cl^- > F^- > Br^-$.

This result reflects the formation of stable monofluorophosphoric acid, which complexes F^- and decreases its corrosivity. The following equilibrium is established:

$$H_3PO_4 + HF \rightleftarrows H_3PO_3F + H_2O$$

In 30% and 50% H_3PO_4 the fluorophosphate complex hydrolyzes and yields free active F^- which promotes corrosion.

Effect of Temperature--A rise in temperature increases the rate of the chemical reactions that occur in the acidulation of the rock and the concentration of the acid. Higher temperatures in the reactor accelerate the corrosion of steel agitators and pumps, and higher temperatures in the concentration stage lead to increased corrosion in heat exchangers, pipes, and pumps. To minimize corrosion, nonmetallic materials are used wherever possible; these include impregnated impervious graphite, carbon bricks, Teflon coatings, and asbestos-filled phenolic resins.

Operation at elevated temperatures also results in scale formation on heat-transfer surfaces.

Breakdown of the passive state may occur at elevated temperatures. For example, type 316 stainless steel is resistant to 85% H_3PO_4 up to about 90°C, but at higher temperatures the passive layer is damaged and corrosion increases.

Effect of Agitation--Agitation is any operation that results in movement of a fluid with respect to a static or moving solid surface, such as flow of a liquid in a pipeline or circulation of liquid by a pump impeller. Agitation produces high velocity, turbulence, impingement, cavitation, and erosion; all of these increase corrosion. The destructive effect that results from the combination of mechanical wear and electrochemical corrosion usually is greater than the sum of the two factors acting separately.

The abrasive solids, gypsum crystals, silica, and unreacted phosphate rock in the reactor slurry which contains about 35% solids, severely attack agitators, pump impellers and casings, and pipes. Erosion corrosion is a localized form of corrosion that is frequently encountered in the WPA acidulation stage and results from the high level of corrosive impurities, such as Cl^-, high temperature, and high liquid velocity. It is characterized by the appearance of grooves, gullies, and waves on the metal surface, usually in a directional pattern.

Passive alloys such as stainless steels owe their corrosion resistance to a protective oxide film. The ability of these films to protect the alloy depends on their resistance to mechanical wear and their rate of regeneration when destroyed or damaged. The condition of the protective film depends on its interaction with the WPA constituents, such as Cl^-, F^-, and oxidizing agents.

Effect of Organic Matter--Phosphate rock contains organic matter from fossil organisms, but its nature is not clearly defined. Its amount ranges from 0.5% to 2.3%, organic carbon. Part of the organic matter may have been introduced as flotation agents that were adsorbed during beneficiation of the phosphate rock. Chemicals that control foaming, such as amines, fatty acids, and esters, that are added in the acidulation step also contribute organic matter.

The effects of these different kinds of organic matter on corrosion in WPA have not been investigated thoroughly. They may affect corrosion in several ways:

1. By forming films of organic matter on metallic surfaces and decreasing or increasing corrosion according to their chemical nature and physicochemical properties such as adsorption.

2. By reacting with corrosive constituents of the acidulation system to change the redox potential of the slurry and the potential of the stainless steel.

Corrosion Testing in WPA

Corrosion is one of the major problems in the production, storage, and transportation of WPA, and instances of corrosion in WPA plants and equipment for handling and processing WPA are reported frequently. To minimize or avoid corrosion problems in new WPA plants and to gather information on the corrosion behavior of steels, corrosion studies may be carried out in the framework of the IFDC Fertilizer Technology Division through use of the present instruments and facilities.

Corrosion studies can be made for the following purposes:

1. To assess the corrosion characteristics of phosphate rocks indigenous to interested countries,

2. To obtain data on the influence of impurities and operating conditions on corrosion in WPA,

3. To evaluate the corrosion resistance of different stainless steels, and

4. To evaluate techniques for minimizing corrosion in WPA plants.

The corrosion tests can be performed at the following three levels:

1. Laboratory tests,

2. Tests in the bench-scale wet-process phosphoric acid unit (BSWPA), and

3. Tests in the WPA pilot plant (PPWPA).

Laboratory Tests--Corrosion tests in the laboratory are based on weight-loss and electrochemical techniques that are discussed in Chapters 5 and 6.

These tests can be made with synthetic solutions to evaluate separately the different parameters of corrosion such as impurities or operating conditions or with solutions produced in the BSWPA, the WPA pilot plant, or even industrial plants.

Simple and fast weight-loss tests can be made by immersion of specimens of several steels in 30% P_2O_5 phosphoric acid solutions containing measured amounts of an impurity, such as Cl^-. The tests should be conducted under constant conditions of type of vessels, amount of solution, temperature, exposure conditions, and time so that the only variable is the concentration of the impurity. Results of such tests will yield comparable data on the effect of the same impurity on the behavior of different steels or on the effect of different impurities on the same steel. It should be borne in mind that the results obtained are affected by the test conditions and that when the conditions are changed a new set of data will be obtained that is similar in trend and magnitude to the previous set but not strictly comparable.

The Potentiodyne Analyzer or a similar recording potentiostat (see section "Corrosion Measuring Instruments) can be used to determine the behavior of different steels in the acid prepared from a specific rock or for evaluating the influence of increasing levels of an impurity such as Cl^- in a specific acid. Preparation of an anodic polarization curve for each steel or each Cl^- level will yield a family of curves on the same recorder paper, and the electrochemical parameters of the curves can be compared directly. Corrosion rates can be calculated from polarization curves by the methods described in Chapter 6. In addition, these results can be compared with results obtained with the corrosion rate meter and weight-loss measurements. These measurements must be made with the same steel electrodes or with small strips or rods of a steel having the same chemical composition and metallurgical properties as those of the steel used for recording polarization curves.

The following set of laboratory corrosion tests in 30% P_2O_5 acid are recommended:

1. Influence of chloride ion. Chloride ion may be added as HCl or NaCl.

2. Influence of fluoride ion alone and with complexing agents such as Si^{+4} or Al^{+3}. Fluoride may be added as HF or H_2SiF_6.

3. Influence of free H_2SO_4.

4. Influence of oxidizers such as Fe^{+3} or NO_3^-, by addition of $FeCl_3$ or HNO_3.

5. Influence of temperature.

<u>The Bench-Scale Wet-Process Acid Unit (BSWPA)</u>--The IFDC BSWPA unit was set up to evaluate the behavior of different phosphate rocks in the production of wet-process phosphoric acid

by the dihydrate process. Phosphate rocks with different mineralogical and chemical composition can be characterized and acidulated to produce filter-grade phosphoric acid. The BSWPA unit was designed for production-oriented research and has a capacity of 100-150 g P_2O_5/hour. A diagram of the unit is shown in Figure 14. The equipment is divided into three sections: feed, reaction, and filtration. The equipment and operation of this unit are described in the February 1979 Progress Report of the Fertilizer Technology Division and the BSWPA manual.

Operation of the unit simulates the process conditions encountered in a typical dihydrate process phosphoric acid plant. Weight-loss corrosion tests are made on stainless steels in the BSWPA unit to evaluate the corrosion characteristics of acids made from phosphate rocks from developing countries. The corrosion specimens are blades of the impeller that agitates the slurry in the reactor.

Typical corrosion rates of stainless steels in the reactor are summarized in Table 5 which shows that the corrosion resistance of the stainless steel specimens tested in the BSWPA unit increases in the order 316 < 317L < Alloy 20 Cb-3 < JS 700. For comparison purposes, results are included of corrosion tests in a primary digestion tank of a WPA plant that operated at a temperature range of 77°-84°C for 96 days with moderate aeration but vigorous agitation. Corrosion rates in the plant were higher, as should be expected, because of the more severe hydrodynamic conditions.

The high-alloyed austenitic stainless steels listed in Appendix N are recommended for testing in the BSWPA unit. These alloys are produced by American and European firms and have been developed for acid service, several of them especially for WPA.

The redox potential of the filter acid is measured with an electrode couple of Pt-SCE on aliquots taken after the filtration of the gypsum. The results indicate the oxidizing power of the filter acid and the probable effect on the corrosion behavior of the steel.

A program of corrosion studies in the BSWPA unit is suggested in Table 6. This program is flexible and can be arranged to suit the parameter being studied and the time available.

Corrosion rates can be measured by weight loss, with the corrosion rate meter, and with the Potentiodyne Analyzer. For reliable and reproducible corrosion rates from weight losses, the samples should be exposed for at least 3 days and for two periods of immersion for each level of impurity. When shorter tests must be made because of the lack of time, the reproducibility of the results should be determined.

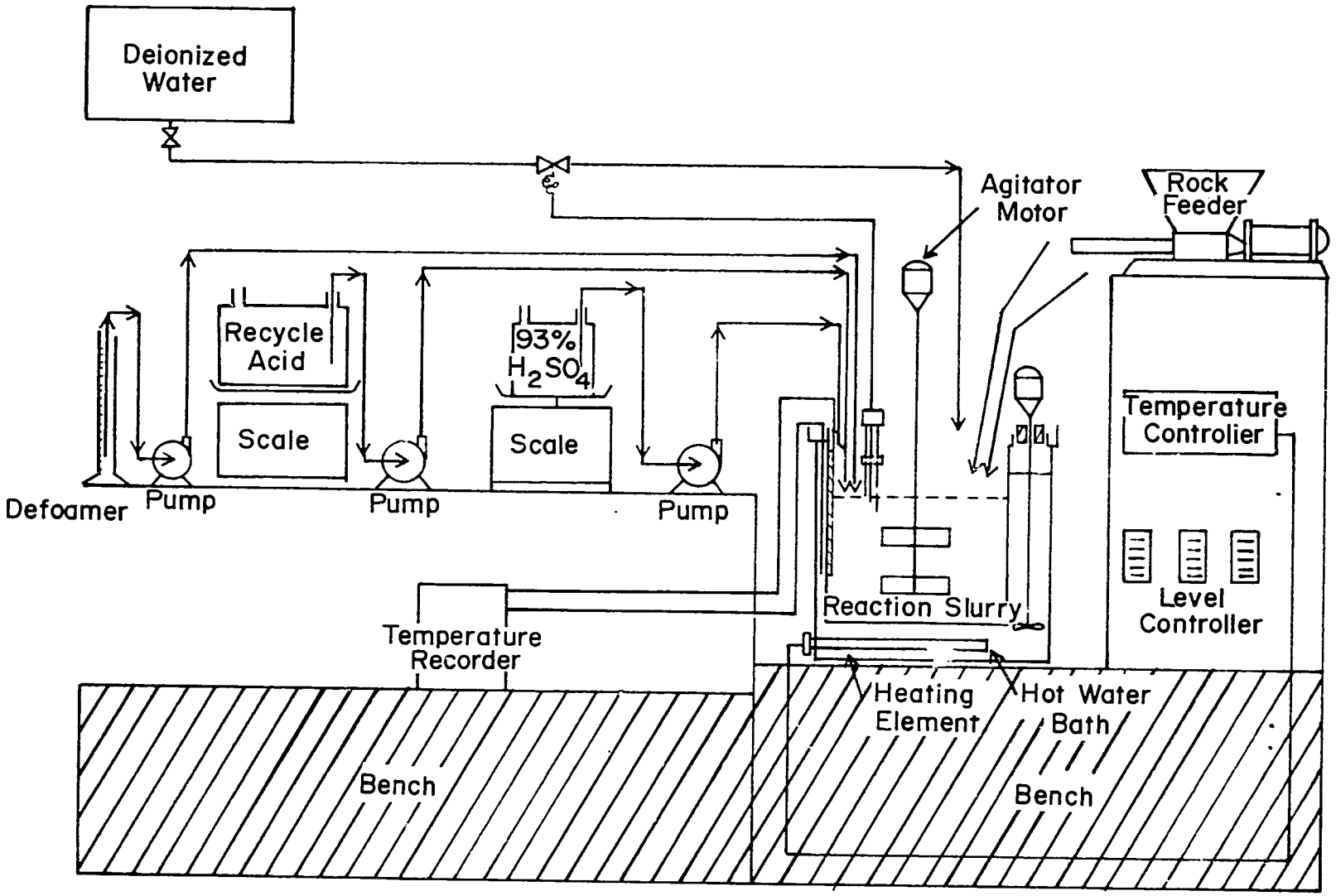


Figure 14. Schematic Diagram of the IFDC Bench-Scale Wet-Process Phosphoric Acid Unit.

Table 5. Typical Corrosion Rates of Stainless Steels During Wet-Process Phosphoric Acid Production

Stainless Steel	Tests at the BSWPA Unit[a]			Plant Test in WPA Reactor[c]
	Position of Specimen[b]	Corrosion Rates, mmpy		Corrosion Rates, mmpy
Alloy 20 Cb-3 (Carpenter Technology Corp.)	Top	0.040	0.042	0.17
	Bottom	0.044	0.055	
JS700 (Jessop Steel Company)	Top	0.025	0.026	
	Bottom	0.026	0.029	
AISI 317				0.55
AISI 317L	Top	0.037	0.046	
	Bottom	0.039	0.051	
AISI 316	Top	0.11	0.14	1.2
	Bottom	0.11	0.13	

a. Results of tests carried out in the BSWPA Unit reactor, during acidulation of Florida phosphate rock.
b. There are two rows of blades on the agitator, top, and bottom.
c. Source: The International Nickel Co., Corrosion Resistance of Nickel-Containing Alloys in Phosphoric Acid, Corrosion Engineering Bulletin, No. 4, 1966, p. 16.

Table 6. Program for Testing the Influence of Impurities on the Corrosion of Stainless Steels in the BSWPA Unit

Order of Test	Impurity	Level, % (in Reaction Slurry)	Source	Addition Procedure	Amount	Chemical Analysis
1	H_2SO_4	2.0	Present	Present		Quality Control Lab.
2	H_2SO_4	4.0	Feed H_2SO_4	By operational change		Quality Control Lab.
3	F^-	~1.6	Phosphate rock			Thornton Analytical Lab.
4	F^-	2.0	48% HF	Proportioned and fed with recycle acid	Additional 0.4%	Thornton Analytical Lab.
5	F^- ($+Si^{+4}$)	2.0	Na_2SiO_3 soln.	Proportioned and fed with sulfuric acid	F additional 0.4% Si^{+4} equiv. to F^-	Thornton Analytical Lab.
6	F^- ($+Al^{+3}$)	2.0	$Al(OH)_3$	Proportioned and fed with sulfuric acid or recycle acid	F additional 0.4% Al^{+3} equiv. to F^-	Thornton Analytical Lab.
7	Cl^-	0.05	NaCl	Proportioned and fed with sulfuric acid		Quality Control Lab.
8	Cl^-	0.3	NaCl	Proportioned and fed with sulfuric acid		Quality Control Lab.
9	$S^=$	0.2	Na_2S	Proportioned and fed batchwise by hand		Thornton Analytical Lab.
10	$S^=$	0.5	Na_2S	Proportioned and fed batchwise by hand		Thornton Analytical Lab.

Types 316 and 317L stainless steels are recommended for tests in the reactor and types 304 and 316 for tests with the electrochemical instruments. The effects of impurity should be tested at a minimum of two levels above and below those expected in commercial acid. The effect of fluorine should be tested by addition of HF with and without Si and Al compounds to complex the F^-. To ensure that these compounds react with F^-, laboratory measurements should be made of their dissolution in 30% P_2O_5 acid containing 2% F^- added as HF. The formation of complexes can be determined by measurements with fluoride-specific electrodes.

The amounts of the impurities in the reactor acid should be determined before and after the tests. The suggested sequence of testing, times of weighing, and times of addition of impurities are shown in Figure 15.

WPA Pilot Plant--The IFDC WPA pilot plant, Figure 16, is intended to simulate industrial operating conditions closely. The results obtained from this pilot plant will be used in the design and operation of industrial-scale units. Pilot-plant tests generally give highly reliable and directly useful information on corrosion.

The capacity of the IFDC WPA pilot plant is about 10 kg of rock per hour. In addition to filter acid production, the plant is equipped to clarify and concentrate the acid. Wet-process phosphoric acid containing up to 54% P_2O_5 can be produced.

The testing techniques, weight loss and electrochemical, mentioned in this manual, can be applied in the WPA pilot plant. Devices and procedures for exposure of specimens in pilot and industrial plants are described in ASTM standard G4-68. Corrosion rates can be measured by exposing suitable specimens in different sections of the pilot plant or by introducing steel electrodes for determining polarization curves and obtaining corrosion rates. The specimens should be held firmly in place and should be protected against mechanical damage. Electrical insulation with an acid-resistant material should be provided to prevent galvanic corrosion.

Special specimens should be tested to determine the effect of welding, soldering, heat treatment, and mechanical stressing.

Possible side effects on the test specimens, such as gypsum deposition, crevice corrosion under specimens' holders, accumulation of corrosion products, and galvanic contacts, should be taken into account when evaluating the test results. Sometimes it is useful to make color photographs of the specimens before exposure, after removal, and after cleaning. Figure 17 shows corrosion specimens after they have been exposed to wet-process acid made in a pilot plant.

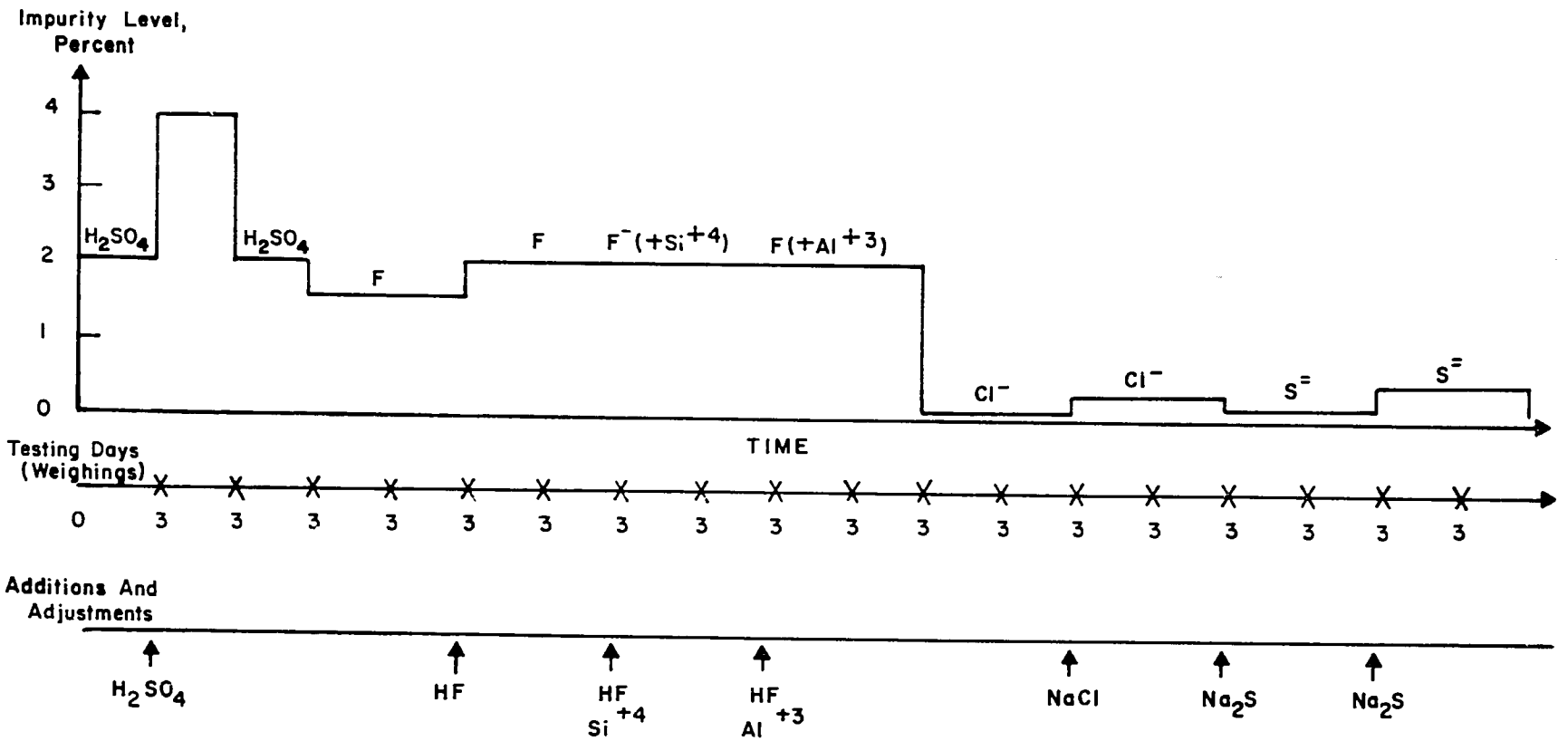


Figure 15. Program for Testing the Influence of Impurities on Corrosion in the Bench-Scale Wet-Process Phosphoric Acid Unit. Testing Sequence and Procedures.

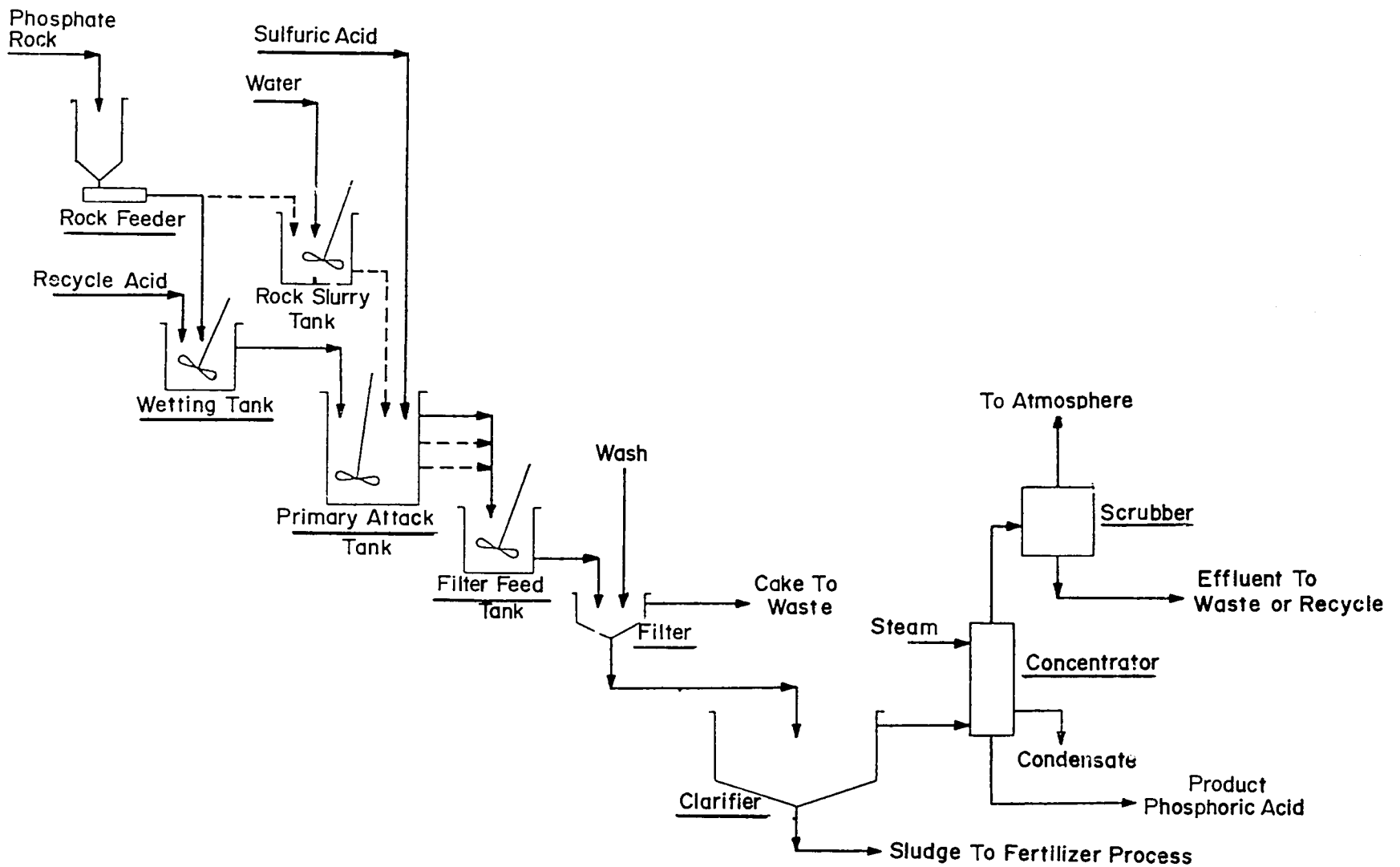


Figure 16. IFDC Wet-Process Phosphoric Acid Pilot Plant.

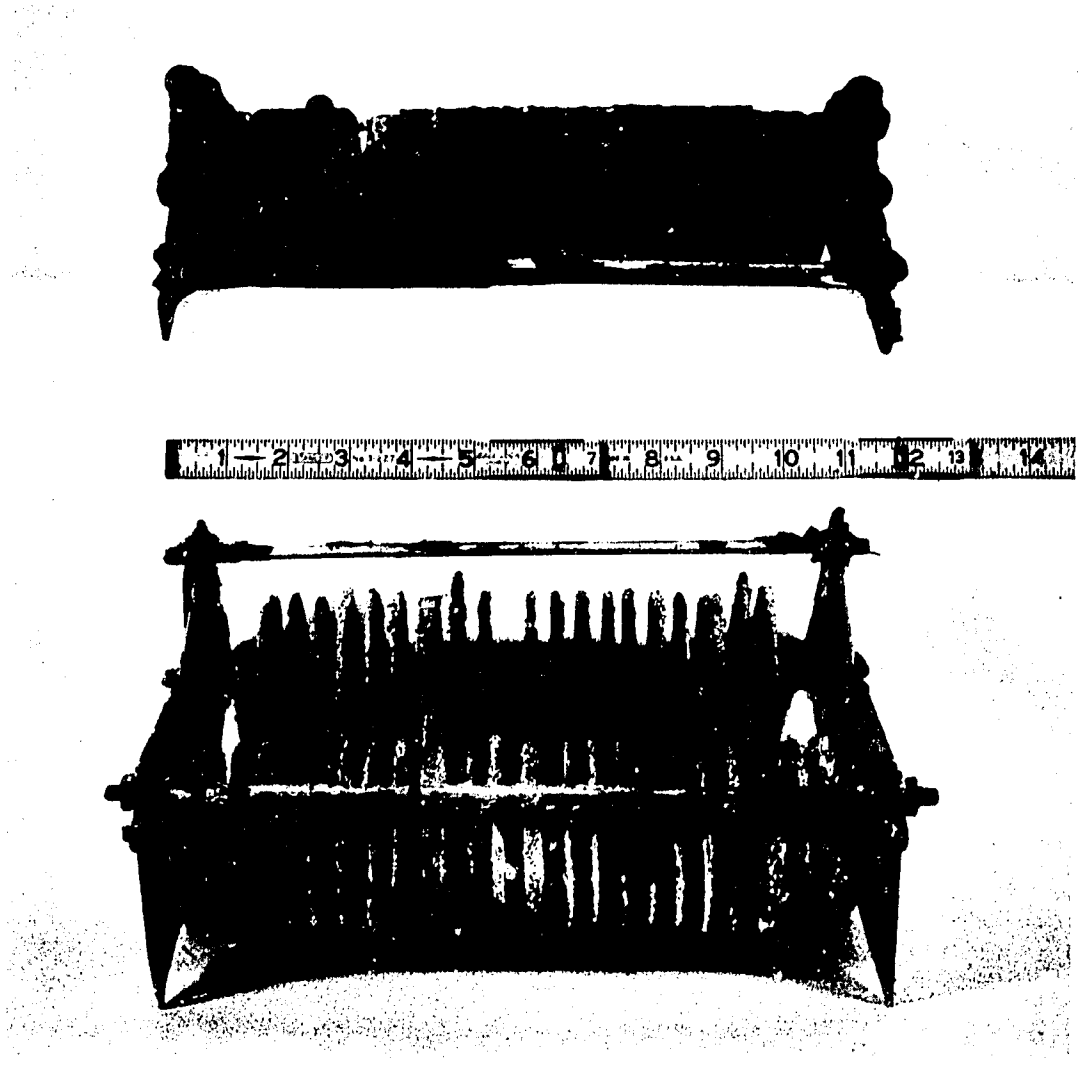


Figure 17. Corrosion Specimens Tested in a Pilot Plant for Producing Wet-Process Phosphoric Acid by the Foam Process.

Corrosion studies in the pilot plant may be made for a number of purposes including:

1. Determination of the influence of corrosive impurities in phosphate rock, by adding additional amounts of impurities or corrosion-reducing additives, such as adding active silica to the rock feed.

2. Identification of erosion-corrosion phenomena in the reaction system, through use of detachable pipe sections to be cut and examined after testing or by attaching pumps fitted with interchangeable impellers made of different stainless steels.

3. Determination of the effect of free H_2SO_4 on corrosion by changing the ratio of H_2SO_4 to rock.

4. Use of oxidizers, such as HNO_3 or cupric salts, to decrease corrosion.

5. Application of anodic protection of chemical equipment.

6. Determination of the resistance of nonmetallic materials, such as plastics, plastic coatings, rubber lining, and acid-resistant bricks.

Corrosion Control in WPA Industry

Although phosphoric acid is not a particularly corrosive chemical, severe corrosion problems are encountered in WPA plants. These problems are related to the corrosive and erosive impurities present in the process systems and to the strong hydrodynamic operating conditions prevailing in the plants. These conditions include temperatures from 50° to 120°C to dissolve the ground phosphate rock or to concentrate the acid to 52% P_2O_5 or even higher to produce superphosphoric acid.

The chemical, mechanical, and thermal factors and their influence on WPA corrosion were discussed in detail in Chapter 7. The general principles and methods applied in control and prevention of corrosion to increase efficiency and lower production costs were described in Chapter 3.

The corrosion problems that arise in the production and use of WPA fall into three groups, those in the production, transport and storage, and application of the final products, including mixed fertilizers.

To minimize these problems, a wide variety of materials of construction are at the disposal of the plant and equipment designers. These materials include corrosion-resistant metals and alloys; plastics (thermoplastics and reinforced thermosets); rubbers, particularly as linings; alumino-silicate, acid-resistant bricks; carbon bricks for lining vessels walls and bottoms; and impervious impregnated graphite for heat-exchanger tubes.

Phosphate rocks are subjected to beneficiation treatments to raise their grade, increase their reaction efficiency, and lower their corrosiveness. Thus, the rock may be calcined to destroy its organic matter and decompose carbonates. Washing with fresh water will lower the Cl^- content and make the rock less corrosive if the chloride is soluble. A Cl^- content above 0.05% usually cannot be tolerated in WPA plants with equipment made of type 316 stainless steel, and rocks with a Cl^- content above 0.3% may cause severe corrosion in equipment fabricated of high-alloy stainless steel of the general composition, 20 Cr, 25 Ni, 3 Mo, 1.5 Cu.

Erosion corrosion occurs in plants operating with siliceous rocks that contain hard and dense forms of silica, such as quartz, and other inert components that are not attacked during acidulation. Erosion corrosion will occur also in equipment fabricated from type 316 or high-alloy stainless steels (see Bibliography) that handle rock high in Cl^-. The Cl^- causes electrochemical breakdown of the natural steel passive state and promotes active dissolution of the components of the steel. Under these conditions, the erosive solids suspended in the reaction slurry and driven past the steel surface or impinging on it act synergistically and lead to rapid failure by erosion corrosion. Agitators in rock digesters and circulation pumps fail often in plants with either high-chloride rock or vigorous agitation. A temporary solution may be the use of rubber-lined carbon steel agitators and pumps with easily replaceable sleeve-type linings.

Pumps that circulate slurries from digesters to filters are particularly subject to erosion corrosion: the plate and blades of the pump impeller are badly corroded, and the surfaces are eaten away in a regular geometrical pattern. To minimize these effects, the impellers should be properly designed, cast, and treated thermally to produce a fine granular structure in the metal and release residual stresses, and high slurry velocities should be avoided in the plant operation.

In plants handling rocks low in silica, reactive types of silica such as diatomaceous earth or siliceous clays usually are added to obtain a favorable $(Si + Al)/F_6$ ratio (see Appendix M) to complex the free hydrofluoric acid and minimize its adverse effect. Plants operating with rocks high in chloride should use equipment made from nonmetallic materials, such as polypropylene filters and piping, rubber-lined steel digesters, tanks, agitators, and many other plant vessels.

Concentrated sulfuric acid can be handled in carbon steel equipment at ambient temperature. Corrosion of this metal is relatively slow because of the formation of a protective layer of iron sulfate, but with less concentrated acid (77% and below) and with elevated temperatures corrosion-resistant steels should be used.

Production of fertilizer from phosphoric acid requires concentrations in the range of 58%-75% H_3PO_4 (42%-54% P_2O_5). Filter acid, 42% H_3PO_4 or 30% P_2O_5, is concentrated by direct or indirect evaporation with conventional heat sources in different processes and in different forms of equipment. The main problems are scaling and corrosion of heat-transfer surfaces by chlorine and fluorine compounds, especially when processing rocks with unfavorable Si:F ratios. The vapor phase carries suspended fumes and mists containing small amounts of SiF_4, HF, HCl, and entrained H_3PO_4, H_2SO_4, and H_2SiF_6 that are highly corrosive to hot surfaces.

Heat-exchanger tubes are made of high-alloy stainless steels or graphite. The shells are usually stainless steels, or they are lined with hard rubber that is resistant to the elevated temperature used in the concentration operation. Pumps are fabricated of high-alloy stainless steels such as alloy 20 and its European equivalents (see Appendix N). The pump components are carefully cast and annealed to prevent intergranular corrosion and stress corrosion in plant operation.

Types 316 and 316L stainless steels and rubber linings are widely used for storage tanks and for tanks for sea, road, and rail bulk transport of phosphoric acid. To avoid solidification of the acid, insulated tank cars and heating elements made of type 316 stainless steel are employed. Severe corrosion has occurred in such tanks, mainly as localized attacks on tank bottoms under sludge and gypsum deposits.

Plastic materials such as polyvinyl chloride, polyethylene, and fiberglass epoxy or polyester (FGR) are being used for containers and pipes, up to their temperature limitations.

Anodic protection systems have been installed in storage and transport tanks to prevent corrosion, particularly pitting corrosion. Cathodic protection of carbon steel tanks for storage of merchant-grade acid and addition of corrosion inhibitors to phosphoric acid have been suggested (see Bibliography), but so far their use has not been consistently accepted in industrial operations.

WPA is used for the production of many dry and liquid fertilizers--triple superphosphate, ammonium phosphates, and liquid mixed fertilizers. The usual material of construction for equipment applied in these processes is type 316 stainless steel.

Most phosphate fertilizers are applied as dry powders or granules by ground-operated equipment such as spinners and spreaders made of carbon steel that is protected by paint or a plastic coating that is resistant to the physical and chemical effects of the fertilizer and to atmospheric and soil conditions. Liquid mixed fertilizers are transported in tank trucks or "nurse" tanks and applied by spraying from tanks. Since these fertilizers can be corrosive to carbon steel, cast iron, and aluminum, type 316 stainless steel is often used for tanks and fittings, and more corrosion-resistant nickel-base alloys are used for pumps, valves, and other moving parts. When unneutralized phosphoric acid is applied to alkaline soils, the equipment usually is made of type 316 stainless steel.

Superphosphate is applied from specially fitted airplanes and helicopters in the United States. In Japan, the United Kingdom, and other countries, ammonium phosphate solutions are applied

through sprinklers of irrigation systems. Equipment for this purpose made of carbon steel and galvanized steel are corroded only slightly.

Modern WPA plants and facilities that are constructed from corrosion-resistant materials and that apply recognized methods of corrosion prevention and control can expect prolonged equipment service life and relative freedom from corrosion.

BIBLIOGRAPHY

1. Alon, A., J. Yahalom, and M. Schorr. 1975. "Influence of Halides in Phosphoric Acid on the Corrosion Behavior of Stainless Steel," Corrosion, 31(9):315-319.

2. Anoschenko, I. P., et al. 1974. "Corrosion Studies on Titanium in Phosphoric Acid in the Presence of Oxidizing Cations," Proc. Semin. Electrochem., p. 425.

3. Banks, W. P., and E. C. French. 1967. "Steel in Phosphoric Acid. Anodic Protection for Corrosion Control," Materials Protection, 6(6):48-49.

4. Barber, J. C. 1958. "Corrosion Problems in the Manufacture of Phosphoric Acid from Elemental Phosphorus," Corrosion, 14:357-362.

5. Bernhardsson, S. O., and R. Osterholm. 1978. "A Special Highly Alloyed Steel Used for Heat Exchangers for Phosphoric Acid Concentration," Information Chimie, 176:125-132.

6. Borghese, A. 1977. "Stainless Steel in the Wet-Process Manufacture of Phosphoric Acid," Ion (Madrid), 37(428):149-153.

7. Bradley, J. 1965. "Velocity Effects Upon Corrosion of Austenitic Stainless Steel (304, 316) in Orthophosphoric Acid," Thesis, Washington University, St. Louis, Missouri.

8. Bunger, J. 1955. "Die Corrosion durch Phosphorsaure bei legierten Stahlen und Nickellegierungen," Werkstoffe und Korrosion, 6:369.

9. Champion, F. A. 1965. Corrosion Testing Procedures, 2d ed., John Wiley, New York, New York.

10. Clarke, D. L., and R. C. Williamson. 1971. "Corrosion of Phosphoric Acid Plants," IN Symposium on the Problems of Plant Maintenance, Proceedings No. 122, p. 44-56, The Fertiliser Society, London.

11. "Corrosion Resistance of Haynes Alloys." 1963. Stellite Division, Union Carbide Steel, Corrosion, 19:180t.

12. The International Nickel Co. 1966. "Corrosion Resistance of Nickel-Containing Alloys in Phosphoric Acid, Corrosion Engineering Bulletin, CEB-4.

13. Tennessee Valley Authority. 1977. Corrosion Studies in Phosphoric Acid, TVA Annual Reports, Muscle Shoals, Alabama.

14. Duberhand, D. 1976. "Erosion-Corrosion in Industrial Phosphoric Acid Environment--Technical and Economic Aspects," Ind. Mineral (St.-Etienne, F.) (Spec. No. March 15), p. 201-205.

15. Durgin, C. B., J. H. Lum, and J. E. Malowan. 1937. "The Chemical and Physical Properties of Strong Phosphoric Acids," Trans. Am. Inst. Chem. Engrs., 33(4):643-668.

16. Ebling, H. F., and M. A. Scheil. 1951. "A Standard Laboratory Corrosion Test for Metals in Phosphoric Acid Service," Trans. Am. Soc. Mech. Engrs., 73:975-987.

17. "Economic Effects of Metallic Corrosion in the United States." 1978. Report to the Congress by the National Bureau of Standards, United States Department of Commerce, Washington, D.C.

18. Fisher, A. O. 1966. "Corrosion by Furnace Grade Phosphoric Acid," Materials Protection, 5(3):29-35.

19. Foley, R. T. 1970. "Role of the Chloride Ion on Iron Corrosion," Corrosion, 26:58-70.

20. Fyfe, D., and J. B. Brooks. 1979. "Corrosion and Oxidation in Sulfuric Acid and Phosphoric Acid Manufacture--Case Histories," NACE Corrosion Forum, Atlanta, Georgia.

21. Gami, D. C., and L. Singh. 1977. "Corrosion Problems and Materials of Construction in Phosphate Fertilizer Plants," Chem. Eng. World, 12(6):59-63.

22. Gladkii, I. N., et al. 1977. "Effect of the Diffusion Strengthening of Cast Iron on Its Stability in Concentrated Phosphoric Acid," Zashch. Met., 13(5):581-583.

23. Hart, A. C. 1973. "Electrochemical Behavior of Iron-Nickel-Chromium Alloys in Phosphoric Acid Solutions Containing Added Impurities," Br. Corros. J., 8:66-70.

24. Hein, L. B. 1968. "Removal of Impurities," IN Phosphoric Acid, Vol. I, Part II, A. V. Slack ed., Marcel Dekker, New York, p. 687-708.

25. Ignatov, B. P., et al. 1973. "Use of Inorganic Inhibitors to Protect Titanium from Corrosion in Concentrated Orthophosphoric Acid," Tr. Novocherk Politekh. Inst., 285:41-44.

26. Industry Guide to the Profitable Use of Monsanto Phosphoric Acid. 1970. Technical Bulletin I-239, Monsanto Co., U.S.A.

27. Lehr, J. R. 1968. "Nature of Impurities," IN Phosphoric Acid, Vol. I, Part II, A. V. Slack ed., Marcel Dekker, New York, p. 637-686.

28. Lizlozs, E. A. 1969. "Corrosion Behavior of Types 304 and 316 Stainless Steel in Hot 85% Phosphoric Acid," Corrosion, 25:389-393.

29. Lowe, J. B. 1961. "Corrosion-Generated Hydrogen Explodes in Phosphoric Acid Tank," Corrosion, 17(3):30, 32.

30. Morgan, A. R. 1959. "Corrosion of Types 316 and 317 Stainless Steel by 75% and 85% Phosphoric Acid," Corrosion, 15(July):29-32.

31. Novakovski, V. M., and A. N. Sorokina. 1966. "Model Study of Chloride Pitting in 18-8 Stainless Steel," Corrosion Science, 6:227-233.

32. Oden, L. L., and B. D. Nash. 1974. "Corrosion of Commercial Alloys in Three Environments Simulating Phosphate Rock Acidulation," U.S. Bur. Mines Rep. Invest. No. 7898, 10 pp.

33. Pelitti, E. 1968. "Corrosion and Materials of Construction," IN Phosphoric Acid, A. V. Slack, ed., Vol. 1, Part 2, p. 827, Marcel Dekker, Inc., New York, New York.

34. Riggs, O. L. 1963. "Effect of Hydrogen Halides on Anodic Polarization of Stainless Steel," Corrosion, 19:180t-185t.

35. Riggs, O. L. 1970. "Cathodic Protection of Carbon Steel in Phosphoric Acids," Materials Protection and Performance, 9(10):21-26.

36. Schorr, M. 1971. "Corrosion and Electrochemical Behavior of Austenitic Stainless Steel in Phosphoric Acid," M.Sc. Thesis, Technion-Israel, Institute of Technology, Israel.

37. Schorr, M. 1978. "Influence of Fluoride in Phosphoric Acid on the Corrosion Behavior of Austenitic Stainless Steel," Extended Abstracts, The International Congress on Metallic Corrosion, Brazil.

38. Shibad, P. R., and J. Balachandra. 1974. "Corrosion of Constructional Materials in the Treatment of Rock Phosphate with Sulfuric Acid. I. Corrosion of Iron and Nickel-Base Alloys," Proc. Semin. Electrochem., p. 408-414.

39. Sidberger, T., and S. Nordin. 1978. "Corrosivity of Wet-Process Phosphoric Acid," Corrosion, 34:16.

40. Smith, A. J., and J. D. Hatfield. 1970. "Free Corrosion of Pure Iron by Phosphoric Acid," Corrosion, 26(8):246-249.

41. Stainless Steels in Phosphoric Acid Industry. 1972. A literature review (IMI internal publication).

42. Streicher, M. A. 1958. "Corrosion of Stainless Steels in Boiling Acids and Its Suppression by Ferric Salts," Corrosion, 14:59t-70t.

43. Suzuki, T., et al. 1973. "Composition of Anolyte Within Pit Anode of Austenitic Stainless Steels in Chloride Solution," Corrosion, 29:18-22.

44. Uhlig, H. H. 1971. Corrosion and Corrosion Control, 2d ed., John Wiley, New York, p. 8.

45. Varsanyi, A., E. B. Winn, and P. H. Peng. 1978. "Bench-Scale Studies of Utilization of Problem Rocks in Wet-Process Phosphoric Acid Production," IN ISMA Technical/Economic Conference, p. 133-150, Orlando, Florida.

46. Vreeland, D. C., and S. H. Kalin. 1956. "Corrosion of Metals by Liquid Fertilizer Solutions," Corrosion, 12:569t-575t.

47. Wallen, B., and I. Andersson. 1977. "Transport of Wet-Process Phosphoric Acid--Corrosion Studies and Experiences," Proceedings Marichem 77, p. 171-183, Hamburg, Federal Republic of Germany.

48. Wallen, B., and I. Andersson. 1979. "Transport of Wet-Process Phosphoric Acids Containing Low Amounts of Impurities," Paper presented at Marichem 79, Monte Carlo, Monaco.

49. Yates, L. D., ed. 1951. Corrosion Tests of Metals and Ceramics, Chemical Engineering Report No. 9, Tennessee Valley Authority, Muscle Shoals, Alabama 35660, U.S.A.

APPENDIX A

Methods and Techniques for Corrosion Testing

Method	Instrument	Application
Visual examination	Magnifying glass	Observation of corroded surfaces
Microscopic examination	Binocular microscope Metallurgical microscope	Examination of localized corrosion
Weight loss	Analytical balance	Corrosion rate measurements
Electrochemical polarization	Potentiostat, potentiodyne analyzer, corrosion rate meter (Petrolite), corrater (Magna)	Simulation of the electrochemical process; influence of impurities in chemical systems
Potential measurements (including redox potential)	Potentiometer, voltmeter	Determination of corrosion tendency
Conductivity	Conductometer	Determination of solution conductivity
Electrical resistance	Corrosometer (Magna)	Corrosion control in aqueous systems
pH	pH meter	pH determination of fertilizer solutions
Oxygen consumption	Oxygen analyzer	Determination of corrosion in water
Chemical analysis	Analytical instruments (wet and instrumental analysis)	Corrosion product analysis
Electromagnetic	Thickness gauge	Measurement of thickness of organic coating on ferrous metals

APPENDIX B

Sources of Information on Corrosion Control and Corrosion Testing

1. Technical Organizations

   a. National Association of Corrosion Engineers (NACE), P.O.B. 896, Katy, Texas 77450; telephone (713)492-0535. Technical Practices Committee T-5 deals with corrosion problems in the process industries, including fertilizer industry.

   b. American Society for Testing and Materials (ASTM), 1916 Race Street, Philadelphia, Pennsylvania 19103. ASTM Committee G-1 deals with corrosion of metals. Subcommittee G01.11 deals with electrochemical measurements in corrosion testing.

   c. American Society of Metals (ASM), Metals Park, Ohio 44073; telephone (216)338-5151.

   d. National Bureau of Standards (NBS), Institute for Materials Research, Corrosion and Electrodeposition Department, Gaithersburg, Maryland, Washington, D.C. 20234.

   e. American Petroleum Institute (API), 2101 L Street, NW, Washington, D.C. 20037.

   f. American Iron and Steel Institute (AISI), 1000 16th Street, NW, Washington, D.C. 20036; telephone (202)452-7100.

2. Abstracts

   a. NACE Bibliographic Surveys of Corrosion, Houston, Texas, 1945-59.

   b. NACE Corrosion Abstracts Yearbooks, Houston, Texas, 1960-80.

   c. Abstracts of the World Corrosion Control Literature. Includes an alphabetic index of subjects in each bimonthly issue and a full index in the November issue of each year. Section 2 of the topical index headings comprises corrosion testing. Section 4.4 deals with corrosion in inorganic chemicals, including fertilizer intermediates and products. Section 7.6 deals with corrosion in process equipment, e.g., agitators, digesters, filters, and section 8.1 presents corrosion in chemical manufacturing.

   d. Corrosion Abstracts, 1958-78. Swedish Corrosion Institute, Stockholm, Sweden.

   e. Fertilizer Abstracts, 1968-80. TVA National Fertilizer Development Center, Muscle Shoals, Alabama, United States. Each annual volume includes a subject index. Relevant subjects are corrosion, equipment, materials, plants, etc.

APPENDIX B

Sources of Information on Corrosion Control and Corrosion Testing
(Continued)

3. Technical Journals

a. Corrosion, NACE

b. Materials Protection, NACE

c. Corrosion Science

d. British Corrosion Journal

e. Corrosion et Anticorrosion (French)

f. Materials Engineering, Reinhold Publishing

g. Corrosion y Proteccion (Spanish)

h. Electroquimica e Corrasao (Portugese, Brazil)

i. Corrosion Engineering (Japanese)

APPENDIX C

Fertilizer Intermediates and Products[a]

Name	Chemical Formula	Composition, % $N-P_2O_5-K_2O$
Nitrogen Fertilizers		
Urea	$(NH_2)_2CO$	46-0-0
Calcium ammonium nitrate (CAN)	$Ca(NH_4)(NO_3)_3$	25-0-0
Ammonium nitrate	NH_4NO_3	35-0-0
Ammonium sulfate	$(NH_4)_2SO_4$	21-0-0
Ammonium chloride (Asia only)	NH_4Cl	26-0-0
Phosphate Fertilizers		
Single superphosphate		0-18-0
Triple superphosphate		0-46-0
Diammonium phosphate (DAP)	$(NH_4)_2HPO_4$	18-46-0
Monoammonium phosphate (MAP)	$(NH_4)H_2PO_4$	11-52-0
Ground phosphate rock (GPR)		
Potassium Fertilizers		
Potassium chloride	KCl	0-0-60
Potassium sulfate	K_2SO_4	0-0-50
Potassium nitrate	KNO_3	14-0-47
Mixed Fertilizers		
Nitrophosphate		20-20-0
Nitrophosphate		23-23-0
Urea-ammonium phosphate (UAP)		29-29-0
Ammonium polyphosphate (APP)		15-60-0
Ammonium polyphosphate		11-55-0
Nitrate based		20-10-10
Nitrate based		17-17-17
Sulfate based		13-13-13
Urea pipe reactor		28-28-0
Urea pipe reactor (TVA base solution)		35-17-0
Aqueous ammonia		18-0-0
Intermediates		
Hydrochloric acid	HCl	
Sulfuric acid	H_2SO_4	
Phosphoric acid	H_3PO_4	
Nitric acid	HNO_3	
Ammonia (anhydrous)	NH_3	
Aqueous ammonia	NH_4OH	
Sulfur	S	

a. Based on a list prepared by Bill Barnett, Outreach Division, IFDC.

APPENDIX D

Sources of Information on Corrosion Resistance of Materials of Construction

1. Corrosion Guide, Rabald (1968)
2. Corrosion Data Survey, Nelson (1960)
3. Corrosion Diagrams, Berg (1965)
4. Corrosion-Resistant Materials Handbook, Mellan (1976)
5. Materials Selectors (Materials Engineering Journal)
6. Fulmer Materials Optimizer (Fulmer Research Institute, U.K.)
7. American Society for Testing and Materials (ASTM)
8. National Association of Corrosion Engineers (NACE)
9. International Standards Organization (ISO)
10. British Standards Institute (BSI)

APPENDIX E

Literature on Corrosion Control and Corrosion Testing

General

1. Fontana, M. G., and N. D. Greene. 1967. Corrosion Engineering, McGraw Hill, New York, New York.

2. Henthorne, M. 1972. "Corrosion, Causes, and Control," Chemical Engineer, McGraw Hill, New York, New York.

3. National Association of Corrosion Engineers (NACE). 1975. Process Industries Corrosion, Houston, Texas.

4. Cocks, F. H. 1973. Manual of Industrial Corrosion Standards and Control, ASTM Special Technical Publication 534, American Society for Testing and Materials (ASTM), Philadelphia, Pennsylvania.

5. Gackenbach, R. E. 1960. Materials Selection for Process Plants, Reinhold Publishing Co., New York, New York.

6. American Iron and Steel Institute. 1966. Stainless Steel in the Chemical Industry, New York, New York.

7. Shreir, L. L. (ed.). 1976. Corrosion, George Newnes, London, England.

8. National Association of Corrosion Engineers (NACE). 1976. Localized Corrosion, Houston, Texas.

Corrosion Testing

1. Ailor, W. A. (ed.). 1971. Handbook on Corrosion Testing and Evaluation, John Wiley, New York, New York.

2. National Association of Corrosion Engineers (NACE). 1971. "Chapter 15," NACE Basic Corrosion Course, NACE, Houston, Texas.

3. Champion, F. A. 1964. Corrosion Testing Procedures (2d ed.), John Wiley, New York, New York.

4. Fisher, A. O. 1964. Tools and Techniques for Laboratory Corrosion Testing, National Association of Corrosion Engineers (NACE), Houston, Texas.

5. American Society for Testing and Materials. 1978. "Metals--Mechanical, Fracture, and Corrosion Testing; Fatigue; Erosion; Effect of Temperature," Annual Book of ASTM Standards, Part 10, ASTM, Philadelphia, Pennsylvania.

6. Wathter, A., and R. S. Treseder. 1974. "Corrosion Testing Evaluation of Metals for Process Equipment," Chemical Engineering Progress, 63:315-326.

7. Laudruni, R. J., et al. 1969. "Apparatus for Corrosion-Erosion Testing," U.S. Patent 3,228,236. E. I. du Pont de Nemours & Co.

APPENDIX E

Literature on Corrosion Control and Corrosion Testing (Continued)

8. LaQue, F. L. 1967. Corrosion Tests and Service Performance, Relation of Testing and Service Performance, ASTM STP 423, p. 61.

9. Brasunas, A. 1967. "A Critical Review of Reproducibility and Interpretation of Corrosion Test Procedures," Mater. Protec., 6(12):20-24.

10. LaQue, F. L. 1963. "Corrosion Testing," IN Corrosion Resistance of Metals and Alloys, F. L. LaQue and H. R. Copson (eds.), Reinhold, New York, New York.

Electrochemical Techniques

1. National Association of Corrosion Engineers (NACE). 1970. Modern Electrical Methods for Determining Corrosion Rates, NACE, Publication 3D 170, Houston, Texas.

2. Martin, R. C. 1978. Application of Electrochemistry Polarization to Corrosion Problems, Petrolite Company, Houston, Texas.

3. Greene, N. D. 1959. "The Classical Potentiostat: Its Application to the Study of Passivity," Corrosion, 15:369t-372t.

4. West, J. M. 1970. "Applications of Potentiostats in Corrosion Studies," British Corrosion Journal, 5:65-71.

5. Prazak, M. 1963. "Evaluation of Corrosion-Resistant Steels Using Potentiostatic Polarization Curves," Corrosion, 19:75t-80t.

6. Greene, N. D. 1962. "Predicting Behavior of Corrosion-Resistant Alloys by Potentiostatic Polarization Methods," Corrosion, 18:136t-142t.

7. Lizlovs, E. A., and A. P. Bond. 1969. "Anodic Polarization of Some Ferritic Stainless Steels in Chloride Media," J. Electrochem. Soc., 96:574-579.

8. Harrell, J. B. 1975. Modern Applications of Potentiodynamic Data in Research and Industry, Petrolite Corporation, Houston, Texas.

9. Greene, N. D. 1965. Experimental Electrode Kinetics, Rensselaer Polytechnical Institute, Troy, New York.

10. Sudbury, J. D., J. W. P. Banks, and C. E. Locke. 1965. "Anodic Protection of Carbon Steel in Fertilizer Solutions," Mater. Prot., 4(6):81.

11. National Association of Corrosion Engineers (NACE). 1977. Electrochemical Techniques for Corrosion, NACE Unit Committee T-3L, Houston, Texas.

APPENDIX F

List of Equipment for a Corrosion Laboratory for the Fertilizer Industry[a]

Equipment/Instrument	Method/Technique	Application
Dynamic potentiostat including logarithmic converter, recorder and three electrodes corrosion cell, e.g., Potentiodyne Analyzer (Petrolite).	Electrochemical	Prediction of corrosion behavior by polarization curves.
Digital potentiometer	Electrochemical	Determination of metal potential
Reference electrodes: calomel, silver chloride, platinum	Electrochemical	Electrochemical measurements
pH meter (digital)	Electrochemical	pH determination
Conductometer	Electrochemical	Determination of electrolytic conductance of fertilizer solutions
Oxygen analyzer	Electrochemical	Measurement of dissolved oxygen content in aqueous solutions
Corrosion rate meter, e.g., Corrater (Petrolite, Magna), Corrosometer, (Magna)	Electrochemical	Measurements of instantaneous corrosion rate in laboratory and industrial tests
Multimeter	Electrical	Measurements of current, resistance, and potential
Set of calipper, micrometer, meter, etc.	Physical	Geometrical measurements of corrosion specimens
Polishing belt and/or wheel	Physical	Preparation of common specimens
Analytical and industrial balances		Gravimetric corrosion tests

(Continued)

APPENDIX F

List of Equipment for a Corrosion Laboratory for the Fertilizer Industry[a] (Continued)

Equipment/Instrument	Method/Technique	Application
Magnifying glasses	Optical	Observation of surfaces of solid materials before and after exposure
Binocular stereoscopic microscope	Optical	Observation of surfaces of solid materials before and after exposure
Metallographic microscope	Optical	Observation of surfaces of solid materials before and after exposure
Photographic cameras: color (Polaroid) and white and black	Optical	Corrosion failure recording and analysis
Ultrasonic thickness gauge	Ultrasonic	Measurements of equipment wall thickness
Dye penetrants for crack detection	Physical	Corrosion failure analysis
Durometers for plastics (Barcol) and elastomers (Shore)	Physical	Determination of surface hardness of plastics and elastomers before and after exposure to fertilizer solutions
Instruments for evaluation of painting and coatings: thickness gauge, hardness, adherence, porosity, abrasion resistance, etc.	Physical	Evaluation of painting and coatings in laboratory testing and industrial service
Chemical laboratory equipment: glassware, furnaces, tools, chemicals, etc.		Use in corrosion research and testing

a. This is a brief list for a laboratory intended for corrosion research and testing related to the fertilizer industry. Several specific instruments are mentioned, but similar instruments from other manufacturers may also be considered.

APPENDIX G

Selected Standards for Laboratory and Plant Corrosion Testing

NACE TM-01-69 (1976 Revision)	Laboratory corrosion testing of metals for the process industries.
NACE TM-02-70	Method of conducting controlled-velocity laboratory corrosion test.
NACE RP-01-73	Collection and identification of corrosion products.
NACE TM-01-74	Laboratory method for the evaluation of protective coatings used as lining material in immersion service.
ASTM G1-72	Preparing, cleaning, and evaluating corrosion test specimens.
ASTM G3-74	Conventions applicable to electrochemical measurements in corrosion testing.
ASTM G4-68	Conducting plant corrosion tests.
ASTM G5-72	Standard reference method for making potentiostatic and potentiodynamic anodic polarization measurements.
ASTM G15-76	Standard definitions of terms relating to corrosion and corrosion testing.
ASTM G31-72	Laboratory immersion corrosion testing of metals.
ASTM G40-73	Standard definitions of terms relating to erosion by cavitation and impingement.
ASTM G46-76	Examination and evaluation of pitting corrosion.
ASTM D2776-72	Corrosivity of water in the absence of heat transfer (electrical methods).
ASTM D2688-70	Corrosivity of water in the absence of heat transfer (weight loss methods).

APPENDIX H

A Proposal for a Shortened and Simplified Procedure for a Laboratory Immersion Corrosion Test[1]

1. Purpose of the Test--To determine the corrosion resistance of a commercial alloy to certain fertilizer intermediate or product solution.

2. Specimen Preparation--Prepare strip coupons, measuring 50 by 25 by 1.6 mm (2 by 1 by 1/16 in), from a rolled stainless steel sheet, by shearing. Drill a hole 4 mm (5/32 in) in diameter about 3.2 mm (1/8 in) from the center of one short edge of the coupon. Remove by grinding any edge splinters or roughness. Use only those coupons which are free from pits and deep scratches. Brush to remove grit, degrease in hot acetone, dry, and place in a dessicator. Weigh coupons on an analytical balance to the nearest 0.1 milligram. Test stainless steel with a mill surface finish, grade 2B or 2D.

3. Equipment--Use a 500-ml narrow-mouth Erlenmeyer flask or a 500-ml glass beaker. Make a hook of 3-mm glass rod, about 140 mm (5-1/2 in) long, the hook having a radius of about 6.3 mm (1/4 in). This hook supports the specimen in the corrosive medium.

4. Test Solution--Prepare aqueous solutions of the fertilizers being evaluated using commercial fertilizers and distilled water, or take test solutions directly from an industrial or pilot plant. The concentration of the solutions should resemble the range found in industrial practice. Determine their chemical composition, pH, dissolved oxygen content, and electrolytic conductance.

5. Test Conditions--Arrange on a work bench the proper number of identical flasks, two for each steel-fertilizer system. Immerse the coupons in the fertilizer solution, all at the same depth. Use a magnetic stirrer to provide gentle stirring. All the flasks should be kept open to the air and at room temperature. Allow tests to remain undisturbed for 5 days if corrosion rates are lower than 5 mpy or higher than 50 mpy; the test duration may be determined by the following equation: Test hours = 2,000/corrosion rate in mpy. Repeat the test for three periods using fresh solution for each period.

6. Cleaning of the Tested Specimen--Remove the specimen from the solution, clean by scrubbing with a brush or a spatula, under a stream of tap water, depending on the degree of adherence of the corrosion products. Clean in acetone and distilled water, dry, weigh to the nearest 0.1 mg, and record.

7. Calculation of Corrosion Rate--Average the weight loss of duplicate test specimens for each fertilizer solution. Express corrosion rate in mdd units according to the following formula:

$$\text{Corrosion rate} = \frac{\text{Weight loss (mg)}}{\text{Area (dm}^2\text{) x Time (days)}}$$

1. This procedure is based on standards ASTM G1-72, ASTM G31-72, and NACE TM 01-69.

A Proposal for a Shortened and Simplified Procedure for a Laboratory Immersion Corrosion Test[1] (Continued)

Convert to other units as required, using the conversion factors given in appendix H of this manual.

8. Reporting of the Data--Report all important information and data, including: fertilizer solution, degree of purity, concentration and properties, volume of solution, temperature, degree of agitation, equipment used for test, duration of test; partial periods and total, chemical composition, trade name or designation of alloy tested, form, size, area and metallurgical conditions of specimen, description of specimen surface before and after corrosion including corrosion products and effects on the test solution, description of the type of corrosion, and corrosion rates in mdd, mpy, and other units as required.

APPENDIX I

Expressions for Corrosion Rates

Conversion of Corrosion Rate Units

Given Units	Dimensions	Multiplier to Convert to mpy, mils/year
ipy	in/year	1,000
ipm	in/month	12,000
mmpy	mm/year	39.4
μmpy	μm/year	0.039
pmps	pm/sec	1.24
$g/(m^2)(h)$	$g/(m^2)(h)$	$345/D^a$
mdd	$mg/(dm^2)(day)$	$1.44/D^a$
$\mu g/(m^2)(sec)$	$\mu g/(m^2)(sec)$	$1.24/D^a$

a. D is metal density, g/cm^3.

A useful expression for calculating corrosion rate is:

$$\text{corrosion rate (mpy)} = \frac{534 \cdot W\ (mg)}{D(g/cm^3) \cdot A(in^2) \cdot t(h)}$$

where

W = weight loss
D = specimen density[a]
A = specimen area
t = exposure time

(Continued)

APPENDIX I

Expressions for Corrosion Rates (Continued)

Alloy	Density, g/cm^3
Aluminum	
99.0 Al	2.71
Al, 1.0 Mg, 0.6 Si, 0.25 Cr	2.70
Brass	
85 Cu, 15 Zn	8.75
71 Cu, 28 Zn, 1 Sn	8.53
65 Cu, 35 Zn	8.47
Bronze	
95 Cu, 5 Sn	8.86
90 Cu, 10 Sn	8.78
94.8 Cu, 3 Si	8.53
85-90 Cu, 10 Al	7.58
Copper	
99.90 Cu, 0.01 P	8.91
Cupro-Nickel	
90 Cu, 10 Ni	8.93
70 Cu, 30 Ni	8.94
Iron	
94 Fe, 3.5 C, 2.5 Si	7.00
99.94 Fe, 14.5 Si, 0.35 Mn, 0.85 C	7.00
Lead	
99.90 Pb	11.34
Nickel	
99.4 Ni	8.89
67 Ni, 30 Cu	8.84
62 Ni, 30 Mo, 5 Fe	9.24
58 Ni, 17 Mo, 15 Dr, 5 W, 5 Fe	8.94
Steel	
0.20 C, Mn, P, S	7.85
Stainless Steel	
11.50-13.50 Cr, 0.15 C	7.75
14.00-.800 Cr, 0.12 C	7.70
18.00-20.00 Cr, 8.00-12.00 Ni, 0.08 C	7.93
16.00-18.00 Cr, 10.00-14.00 Ni, 2.00-3.00 Mo, 0.08 C	7.98
17.00-19.00 Cr, 9.00-12.00 Ni, 0.08 C, Ti	8.02
19.00-21.00 Cr, 24.00-30.00 Ni, 2.00-3.00 Mo, 3.00-4.00 Cu	8.02
Tantalum	16.60
Tin	7.30
Titanium	4.54

APPENDIX J

Summary of Corrosion Testing Data and Results

1. System
   a. Chemical composition and concentration
   b. Temperature (maximum, minimum, average)
   c. Degree of agitation
   d. Aeration
   e. Other conditions

2. Alloy
   a. Chemical composition
   b. Commercial designation
   c. Producer

3. Weight-Loss Technique[1]
   a. Specimen's shape and dimensions
   b. Surface condition
   c. Exposure conditions
   d. Exposure time
   e. Corrosion rate: mdd, mpy, mmpy

4. Electrochemical Techniques[2]
   a. Potentiometer
      (1) Redox potential; E_{redox}, V
      (2) Null current potential versus SCE; E_sV
      (3) Change of potential versus time; E versus t, V versus h
   b. Corrosion rate meter (Petrolite)
      (1) Null current potential; E_sV
      (2) Corrosion rate, mpy, mdd, mmpy
      (3) Corrosion rate (according to the weight loss of the electrode), mdd, mpy, mmpy

---

1. In accordance with standards NACE TM-01-69 and G1-72 (see Appendix G).
2. In accordance with ASTM standards G3-74 and G5-72 (see Appendix G).

APPENDIX J

Summary of Corrosion Testing Data and Results (Continued)

c. Potentiodyne analyzer (Petrolite)

(1) Corrosion cell electrodes

(2) Mode

(3) Null current potential, E_s V

(4) Primary passivation potential, E_{pp} V

(5) Passive potential, E_p, V

(6) Critical current density, i_{cc} mA/cm^2

(7) Passive current density, i_p mA/cm^2

(8) Anodic Tafel slope, b_a mV/decade

(9) Cathodic Tafel slope, b_c mV/decade

(10) Corrosion potential, E_{corr} V

(11) Corrcsion current density, i_{corr} mA/cm^2

(12) Corrosion rate (from i_{corr}), mdd, mpy, mmpy

APPENDIX K

Chemical Composition of Phosphate Rocks[a]

Constituent[b]	Florida, U.S.A.	North Carolina, U.S.A.	Pesca, Colombia	Hazara, Pakistan	Araxa, Brazil	Sahara, Morocco	Safi, Morocco	Ruseifa, Jordan	Oron, Israel
P_2O_5	31.2	29.7	20.5	28.5	35.5	34.2	32.4	33.4	29.8
CaO	45.0	47.4	29.0	41.9	47.3	50.3	49.9	51.0	51.0
Cl	0.05	0.015	0.001	0.03	0.001	0.02	0.02		0.03
F	3.60	3.53	2.0	2.92	2.54	3.8	4.1	4.2	3.8
SiO_2	9.48	1.73	39.2	23.2	0.41		2.85	4.9	0.68
Fe_2O_3	1.33	0.79	0.8	1.85	2.42	0.22	0.70	0.2	0.2
Al_2O_3	1.76	0.53	1.1	1.0	0.32	0.48	0.40	0.3	0.3
MgO		0.79	0.09	0.13	0.07	0.12	0.70		
Na_2O	0.89	0.98	0.14	0.16	0.03		0.90		
K_2O	0.11	0.17	0.14	0.31	0.10		0.10		
CO_2	3.48	4.18	3.0	1.1	1.7	2.7	4.1	4.5	7.8
Organic C	2.18	1.38	0.3	0.18	<0.1	0.06			0.6
Total S	1.05	1.1	0.1	0.18	1.52		0.20		
	($SO_4^{=}$)	($S^{=}$)		($S^{=}$)	($SO_4^{=}$)				

a. Include rocks from several sources, some of them used in studies on WPA technology and corrosion behavior of steels, conducted by the WPA Group of the Fertilizer Technology Division, IFDC.
b. Figures are given in weight percentage on a dry basis.

APPENDIX L

Materials of Construction and Lining Used in the Phosphoric Acid Industry[a]

Material	Remarks[b]	Typical Application
Elastomers	Natural and synthetic	Membranes behind acid-proof bricks
Neoprene	Synthetic rubber	Equipment lining
Nitrile rubber	Synthetic rubber	Equipment lining
Butyl rubber	Synthetic rubber	Equipment lining
Hypalon	DuPont Co.	Conveyor belts and gaskets
Plastics		
a. Thermoplastics		
Polyvinyl chloride (PVC)	Rigid unplasticized PVC	Piping, small equipment
Polyethylene	High and low density	Piping
Polypropylene		Piping, ducts, scrubbers
Fluorocarbons	Fluoroethylene polymers: Teflon, Kynar, Halar, etc.	At elevated temperatures
b. Thermosets		
Polyester resin	Fiberglass reinforced	Tanks and pipes
Phenolic and furane resins	Asbestos or graphite filled: Haveg, Keebush, Kestra	Top service temperature, 130°C
Epoxy resins	Fiberglass reinforced	Top service temperature, 150°C
c. Coatings		
Phenolic		Hood and duct coating
Penton		Piping
Saran		Piping
Alloys		
a. Stainless Steels		
Austenitic stainless steels	Cr-Ni and Cr-Ni-Mo steels, AISI types 304, 304L, 316, 316L, 317	Equipment handling acid with a low Cl^- content and high SiO_2 content. Tanks, pumps, agitators, filters.

(Continued)

APPENDIX I

Materials of Construction and Lining Used in the Phosphoric Acid Industry[a] (Continued)

Material	Remarks[b]	Typical Application
a. Stainless Steels (cont.)		
High-alloy stainless steels	Cr-Ni-Mo-Cu steels, American and European producers	Equipment handling acid with high Cl content and low SiO_2 content
b. Ni-Base Alloys		
Hastelloy alloys	Stellite Division, Cabot Corporation	Equipment operating at elevated temperature
Monel 400	The International Nickel Co.	Equipment operating at elevated temperature
Inconel 600	The International Nickel Co.	Equipment operating at elevated temperature
Chlorimet 2	The Duriron Co.	Equipment operating at elevated temperature
Chlorimet 3	The Duriron Co.	Equipment operating at elevated temperature
Ceramics	Attacked by HF	
Chemical stoneware		Floor drains
Acid-proof bricks		Tank lining, floor protection
Concrete		Equipment foundations, waste tanks
Carbon bricks		Vessel linings
Graphite	Impervious impregnated: Karbate, Graphilor, Delanium, Diabon	Heat-exchanger tubes

a. Main sources: G. J. Dell, "Construction Materials for Phos-Acid Manufacture," Chem. Eng., April 10, 1967, p. 234; J. J. Pike, "Choosing Materials for Phos-Acid Concentration," Chem. Eng., March 13, 1967, p. 192; D. W. McDowell, "Handling Phosphoric Acid and Phosphate Fertilizers, Parts I and II," Chem. Eng., August 4, 1975, p. 119, September 1, 1975, p. 121; E. Rabald, "Corrosion Guide," Phosphoric Acid, p. 556, Elsevier Publishing Co., Amsterdam, 1968.

b. The remarks include commercial names, producers, and materials characteristics. Specific materials are mentioned, but similar materials from other producers may be suitable also.

APPENDIX M

Calculation of the Complexing Ratio[1] $(Si+Al)/F_6$

1. In the acidulation of phosphate rock, the complexes $SiF_6^{=2}$ and $AlF_6^{=3}$ form

$$6F^- + SiO_2 \text{ gives } SiF_6^{=2}$$
$$114 \qquad 60$$
$$6F^- + \tfrac{1}{2}Al_2O_3 \text{ gives } AlF_6^{=3}$$
$$114 \qquad 51$$

2. In a Florida phosphate rock containing

P_2O_5	F	SiO_2	Al_2O_3	
31.2	3.6	9.5	1.7	%

there are then

$$\frac{3.6}{114} = 0.0315 \text{ moles } F_6$$

$$\frac{9.5}{60} = 0.158 \text{ moles Si}$$

$$\frac{1.7}{102} = 0.0166 \text{ moles Al}$$

3. The complexing ratio $(Si + Al)/F_6$ then is $(0.158 + 0.0166)/0.0315 = 5.5$. Since SiO_2 and Al_2O_3 then are in excess, and if SiO_2 and Al_2O_3 are active, corrosion due to fluorine should not be expected because all F^- will be complexed during acidulation.

For any rock or acid the complexing ratio is:

$$\left(\frac{\%\ SiO_2}{60} + \frac{\%\ Al_2O_3}{102}\right) \Big/ \frac{\%\ F}{114}$$

4. In phosphate rocks with an excess of SiO_2 and Al_2O_3, with respect to fluorine, the complexing ratio is > 1. On the other hand, in rocks deficient in silica and alumina, the complexing ratio is < 1. A simple and rapid test to determine whether silica and alumina are active and react with free hydrofluoric acid should be developed.

---

1. This is a tentative approach that should be critically evaluated before application to assess the corrosivity of phosphate rocks and phosphoric acids.

APPENDIX M

Calculation of the Complexing Ratio[1] $(Si+Al)/F_6$ (Continued)

5. The complexing ratio for filter and concentrated acid should be corrected taking into account fluorine distribution during production. A typical fluorine distribution is given in Table M1.

Table M1. Typical Fluorine Distribution in Phosphoric Acid Production[a]

Fluorine	% of F in Rock
Evolved in reaction section	4-7
In gypsum cake	25-30
Evolved in evaporators	35-45
In product acid	20-30

a. Source: Slack, A. V., ed. 1968. Phosphoric Acid, Vol. 1, Part 1, p. 197, Marcel Dekker, New York, New York.

6. The complexing ratio for different phosphate rocks and filter acids produced at the BSWPA unit is given in Table M2.

Table M2. Chemical Composition of Phosphate Rocks and Filter Acids[a]

	United States									
	Florida		North Carolina		Colombia Pesca		Pakistan Hazara		Brazil Araxa	
	Rock	Acid	Rock	Acid	Rock	Acid	Rock	Acid	Rock	Acid
P_2O_5	31.2	29.4	29.7	31.0	20.5	31.1	28.4	27.8	35.5	32.7
F	3.60	1.38	3.53	1.11	2.0	1.70	2.92	1.98	2.54	0.47
SiO_2	9.48	0.26	1.73	0.11	39.2	0.22	23.2	0.26	0.41	0.06
Al_2O_3	1.33	0.64	0.53	0.28	1.1	1.02	1.0	0.63	0.32	0.008
Complexing ratio	5.4	0.84	1.1	0.47[b]	37.6	3.1	15.4	0.60	0.44	0.26
Acid corrosivity										
AISI type 316 corrosion rate, mmpy	0.12		0.16		0.05		5.71		0.65	

a. Produced in the IFDC BSWPA unit.
b. 0.68 if Mg is considered.

APPENDIX N

Austenitic Stainless Steels and Ni-Base Alloys Recommended for Corrosion Testing in the BSWPA Unit

Trade Name	Producer	Chemical Composition, %					
		Cr	Ni	Mo	Cu	C_{max}	Others
AISI 300 Series							
304		18	8			0.08	
316		18	12	2.5		0.08	
316L		18	12	2.5		0.03	
317		10	14	3.5		0.08	
317L		20	14	3.5		0.03	
High-Alloy							
a. American							
Alloy 20 Cb-3	Carpenter Technology Corp.	21	25	4.5		0.03	0.30 Cb
JS700	Jessop Steel Co.	25	21	4.5		0.03	0.30 Cb
Durimet 20	The Duriron Co.	20	29	2	4		
Worthite	Worthington Industries, Inc. Worthington Steel Co. Division	20	24	3	2		
AL-6X	Allegheny Ludlum Steel Co.	20	24	6			
Inconel 625	International Nickel Co.; Huntington Alloys	22	61	9		0.05	3 Fe, 4 Nb
Hastelloy G	Cabot Corp., Stellite Division	22	Bal.	6		0.05	20 Fe, 2 Co
Hastelloy C-4	Cabot Corp., Stellite Division	16	Bal.	15		0.01	3 Fe, 2 Co
b. European							
UHB 904L	Uddeholm, Sweden	20	25	4.5	1.5	0.02	
Avesta 254 SLX	Avesta, Sweden	20	25	4.5	1.5	0.02	
Avesta 254 SMO	Avesta, Sweden	21.2	17.6	6.1		0.02	0.12 N
2 RK 65	Sandvik, Sweden	20	25	4.5	1.5	0.02	
2 RE 69	Sandvik, Sweden	25	22	2.1			
Sanicro 28	Sandvik, Sweden	27	31	3.5	1.0	0.02	
Uranus B6	Creusot-Loire, France	20	25	4.5	1.5		
Uranus B6 P	Creusot-Loire, France	20	25	4.5	1.5		5.0 W
HV 9A	Usines E. Henricot, Belgium	20	25	4.5	1.5		
Ferralium (Ferritic-Austenitic)	Langley Alloys, U.K.	25	5	2	3		