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FERROUS PIPELINE CORROSION PROCESSES, DETECTION, AND MITIGATION

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LIST OF SYMBOLS

Capital Letters

A = Amperes

A242 = ASTM standard for high strength, low alloy structural steel

A285 = ASTM standard for low to intermediate strength, low alloy steel for pressure vessels

A517 = ASTM standard for high strength, low alloy steels for pressure vessels

A = Exposed area in square feet

AC = Alternating current

Ag = Silver

AGA = American Gas Association

AIME = American Institute of Mining, Metallurgical, and Petroleum Engineers

AISI = American Iron and Steel Institute

Al = Aluminum

API = American Petroleum Institute

As = Arsenic

As_2O_3 = Arsenic trioxide

ASTM = American Society for Testing Materials

AWWA = American Water Works Association

B = Boron

$BaSO_4$ = Barium Sulphate

Br^- = Bromide ion

C = Carbon

°C = Degrees centrigrade

C_a = Aggressor concentration

Ca^{++} = Calcium ion

$CaCO_3$ = Calcium carbonate

$Ca(HCO_3)_2$ = Calcium bicarbonate

$Ca(NO_3)_2$ = Calcium nitrate

$CaSO_4$ = Calcium sulphate

Cd = Cadmium

Cl = Chlorine

Cl^- = Chloride ion

CO_2 = Carbon dioxide

$CO_3^=$ = Carbonate ion

C_P = Passivator concentration

Cr = Chromium

CrO_4^{2-} = Chromate ion

Cu = Copper

$CuSO_4$ = Copper sulphate

DC = Direct current

DOT = Department of Transportation

E = Potential (volts)

E° = Standard half-cell potential for unit activities of reactants and products: function of temperature

E_{corr} = Corrosion potential (volts)

EMF = Electromotive force

F = Faraday's constant (96,500 coulombs/g. equiv. reaction)

°F = Degrees Fahrenheit

F^- = Fluoride ion

Fe = Iron

Fe^{++}, Fe^{2+} = Ferrous ion

Fe^{3+} = Ferric ion

$FeCl_2$ = Ferrous chloride (Lawrencite)

$Fe(OH)_3$ = Ferric hydroxide

Fe_2O_3 = Iron oxide (hematite)

Fe_3O_4 = Iron oxide (magnetite)

Fe_2P = Iron phosphide

H = Hydrogen

H^+ = Hydrogen ion

HCl = Hydrogen chloride (hydrochloric acid)

HCO_3^- = Bicarbonate ion

$HCrO_4^-$ = Bichromate ion

Hg = Mercury

HNO_3 = Nitric acid

HS^- = Bisulfide ion

HVDC = High voltage direct current

H_2 = Hydrogen molecule (gas)

H_2CO_3 = Carbonic acid

H_2O = Water

H_2S = Hydrogen sulfide

H_2SO_4 = Sulphuric acid

H_3BO_3 = Boric acid

I^- = Iodide ion

I-E Curves = Current-potential plots

In = Indium

IR = Current times resistance

J-55 = Alloy tubing specifications

K^+ = Potassium ion

K_a = Constant dependent on metal type

K_n = Constant dependent on aeration of soil

LiCl = Lithium chloride

M = Metal

M^{n+} = Metal ion with a positive charge of n.

Mg = Magnesium

Mg^{2+} = Magnesium ion

$MgCl_2$ = Magnesium chloride

$Mg(OH)_2$ = Magnesium hydroxide (Brueite)

Mn = Manganese

Mo = Molybdenum

N = Normality of a solution

N = Nitrogen

N-80 = Alloy tubing specifications

Na^+ = Sodium ion

NaBr = Sodium bromide

NACE = National Association of Corrosion Engineers

NaCl = Sodium chloride (common salt)

NaF = Sodium fluoride

NaI = Sodium iodide

NAPCA = National Association of Pipe Coating Applicators

NBS = National Bureau of Standards

NH_3 = Ammonia

NH_4^+ = Ammonium ion

NH_4NO_3 = Ammonium nitrate

NH_4OH = Ammonium hydroxide

Ni = Nickel

NO_2^- = Nitrite ion

NO_3^- = Nitrate ion

N_2 = Nitrogen molecule (gas)

O_2 = Oxygen molecule (gas)

OD = Outside diameter

OPS = Office of Pipeline Safety

OH^- = Hydroxide

P = Phosphorous

Pb = Lead

Pt = Platinum

R = Linear corrosion rate (e.g., mpy)

R = Gas constant

Re = Rhenium

R_p = Pitting rate

S = Sulphur

S^+ = Sulphide ion

SCE = Saturated calomel electrode

SHE = Standard hydrogen electrode

Si = Silicon

Sn = Tin

SO_2 = Sulphur dioxide

SO_4^{2-} = Sulphate ion

Sr^{++} = Strontium ion

T = Absolute temperature

Ti = Titanium

TK = Alloy tubing specifications

U = Uranium

UK = United Kingdom

V = Volts

V_m = Molar volume of the metal

Zn = Zinc

Zn^{++} = Zinc ion

Small Letters

a = Activity, equals concentration for ideal mixture

a = Equation constant dependent on alloy

$a^4_{OH^-}$ = Fourth power of the activity of the hydroxide ion

a_{O_2} = Oxygen activities

a_H = Hydrogen ion activity

b = Constant

cm^2 = Square centimeters

cu = Cubic

e^- = Electron

exp = e (base of natural logarithms) raised to the power in the parentheses

ft = Length in feet

g = Grams

i = Current

i_{corr} = Corrosion current, amperes

k = Equation constant

lb/A year = Pounds per ampere year

log = Common logarithm (base 10)

m^2 = Square meter

mA or ma = Milliamperes

mils = Thousandths of an inch

mm = Millimeters

mpy = Thousandths of an inch per year

mV = Millivolts

n = Equation constant dependent on aeration of soil

n = Number of electrons exchanged in the anodic corrosion reaction

ohm cm = Resistivity - electrical resistance of a 1 cm-cube of material

p = Pit depth

pH = Negative logarithm (base 10) of the hydrogen ion

pOH = Negative logarithm (base 10) of hydroxide ion concentration

ppm = Parts per million

psi = Pounds per square inch

Greek Letters

a = Value of η at current $i = 1$

α = Proportional to

β = "Beta constant," Tafel constant, or Tafel slope

y-$Fe_2O_3 \cdot H_2O$ = Gamma ferric oxide monohydrate

η = Overpotential (deviation of potential from the reversible value)

θ = Time in years

ρ = Soil resistivity in ohm-cm

SECTION I

INTRODUCTION

1. Program Objectives

The purpose of this program was to determine the current state of the art of corrosion of ferrous pipelines. This included corrosion mechanisms, frequency and causes of corrosion failure, corrosion mitigation, corrosion detection, and inspection and standards. The program goal was achieved by three separate but interacting paths: (1) a literature survey, (2) a questionnaire, and (3) personal contacts.

2. Literature Survev

Emphasis was placed on corrosion literature published between 1945 and July 1970. Only exceptional publications outside of this period were utilized. The major sources of the corrosion literature were Bibliographic Surveys of Corrosion, Corrosion Abstracts, and Supplements to Corrosion Abstracts, all published by NACE (National Association of Corrosion Engineers, Houston). Other sources were several hundred books, trade and professional journals, symposia and research publications, and Corrosion Control Abstracts (published by Scientific Information Consultants Limited, London).

Corrosion Abstracts comprehensively cover 88 domestic, foreign, and government sources. The Corrosion Control Abstracts are a translation of the Russian abstract journal Referativnyy Zhurnal which covers about 800 worldwide publications.

Approximately 90 percent of the world's corrosion literature From 1945 through 1970 was covered in these series. This amounted to sorting through over 80,000 general corrosion abstracts and papers. Approximately 32,000 of these were from foreign sources. Each abstract that was pertinent to this program was mounted on separate sheets of paper, edited, and key word coded for computer retrieval. This came to a total of 1826 abstracts. Approximately 35 percent of these appeared sufficiently interesting to warrant detailed study of the original works. In those cases the abstracts were further edited or entirely rewritten, and subjective comments were made in the abstract and/or as part of the discussion in the body of this report.

The 1826 abstracts mentioned above were placed on magnetic tape. Thirty-one percent of these were from foreign journals, while the remainder were from domestic sources. Listings of the abstracts grouped by key words and in numerical order are on file at OPS-DOT (Office of Pipeline Safety-Department of Transportation).

Table 1 shows the key words (or key phrases) used! to code or classify the abstracts. The key word code, followed by the authors' names, the literature reference and the abstract itself, was then keypunched on Hollerith cards. All of this information may be recalled on command. Thus one may, for example, recall all abstracts dealing with <u>anaerobic-bacterial-corrosion</u> of <u>carbon-steels underground</u> by asking the computer for those key phrases. The search for these three key phrases is found in Appendix I. Any single key word or combinations of key words may be searched. In addition, all the papers written by an author or groups of authors can be recalled; for example, all the abstracts or papers written by Peabody can be recalled and printed out. Other key words dealing with pipeline corrosion but not listed in Table 1 may also be used to search for abstracts.

The abstracts were numbered sequentially as received. The references in this report use the same abstract numbers as the literature search, e.g., (552) is Reference 552 in the list of references.

A wide range of literature was uncovered. The level of presentation varied the full range from very elementary to very advanced. Many, if not most, of the papers were merely restatements of what was already known. Numerous papers were clearly sales promotions for one company's products or services. Nevertheless, much new information has been uncovered which does not yet appear in any book. This report emphasizes the new information that was considered important.

3. Questionnaire Methods and Responses

The development and response of the corrosion questionnaire was a significant cooperative achievement of the operating industry and the Office of Pipeline Safety.

In the development phase, the entire field of underground and underwater ferrous pipeline corrasion knowledge was outlined. From this was drawn a series of questions on inspection, causes, coatings, cathodic protection, cathodic protection criteria, surveillance, control, maintenance, interference, and research. The questions were chosen to supplement and. expand on the knowledge available from the literature search. The questionnaire **was** then reviewed and expanded by a number of industry and governmental corrosion committees and specialists. The reviews of the

TABLE 1

KEY WORD* CODE FOR COMPUTER RETRIEVAL OF CORROSION LITERATURE

CORROSION MECHANISMS

- Corrosion Mechanisms (gen)
- Uniform Corrosion
- Galvanic Corrosion
- Crevice Corrosion
- Pitting Corrosion
- Intergranular Corrosion
- Selective Leaching
- Stress Corrosion
- Corrosion Fatigue
- Erosion Corrosion
- Hydrogen Effects
- Biological Attack (gen)
- Anaerobic Bacterial Corrosion
- Aerobic Bacterial Corrosion
- Fungal and Other Microbiological Corrosion
- Macrobiological Action
- Evaluation - Corrosion Testing
- Basic Electrochemical Data
- Shielded Areas

ECONOMICS

- Economic Data

CHEMICAL ENVIRONMENT

- Underground
- Soil Resistivity
- Aboveground
- Water
- Seawater
- Oxidizing Agents
- Salts
- Acids - Low pH (<7)
- Alkalies - High pH (>7)
- Organics, Petroleum
- Gases
- Liquified Petroleum Gas
- Anhydrous Ammonia
- Effect of pH (high & low)
- Noble Metal Ions or Fe^{2+}

ELECTRICAL EFFECTS

- External Current
- Interference
- Sacrificial Anode
- Stray Currents
- Anodic Protection
- Anodes
- Polarization

PROTECTION

- Protection Methods (gen)
- Cathodic Protection
- Materials Selection
- Coatings (gen)
- Asphalt Coatings
- Coal Tar Coatings
- Wax Coatings
- Plastic and Other Organic Coatings
- Thin Film Coatings
- Metal Coatings
- Biological Attack of Coatings
- Methods of Applying Coatings
- Paints and Zinc Rich Coatings
- Antibiological Agents
- Inhibitors

PIPELINE OPERATION

- Construction Techniques
- Inspection
- Exterior Defect Detection
- Interior Defect Detection
- Routine Maintenance
- Repairs
- Criteria for Cathodic Protection

TYPE OF ARTICLE

- Experiment
- General Review or Book
- Specific Review
- Theory
- Accidents
- Field Experience
- Rules, Laws, Standards
- News Articles

ALLOY BEING STUDIED

- Carbon Steels
- Wrought Iron
- Cast Irons
- Silicon Irons
- Pure Irons
- Stainless Steels
- Iron Alloys (gen)
- Nonferrous Metals
- Nonmetals

PHYSICAL ENVIRONMENT

- Room Temperature, Pressure
- Effect of Temperature
- Effect of Pressure
- Effect of Velocity
- Effect of Time
- Soil Stress

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* Key words other than those listed may be used to define the retrieval search area.

questionnaire were constructive, and the cooperation was excellent. More than 92 individuals contributed to the questionnaire. A copy of the 21-page questionnaire is contained in Appendix 11.

The response of the operating industry to the voluntary questionnaire was unprecedented for a nationwide survey. Six hundred questionnaires were sent to the operating industry. From this 62.1 percent, or 373 operating companies, responded. Ten and seven-tenths percent of the corrosion research organizations and 9.6 percent of the corrosion consultants responded to the questionnaire. A total of 404 questionnaire responses were received. Eighty-eight percent of the petroleum companies, 59 percent of the gas operating companies, and 53 percent of the water companies responded. The majority of the companies that did not respond were small companies with a limited technical staff who felt that they could not justify the time and expense to respond or that they did not have the necessary corrosion knowledge.

The 373 operating responses were divided as shown in Table 2.

The questionnaire had two types of enswers, numerical and essay. The numerical answers were coded and placed on Hollerith cards for computerized analysis. The computer tabulated the responses and printed a copy of the questionnaire with answers. A separate report was made for:

- The 373 Operating Companies
- Consultants
- Research Organizations
- Other Interested Groups

TABLE 2

OPERATING RESPONSES

Operating Companies	Number of Companies
Gas Gathering	32
Gas Storage Area Gathering	18
Gas Transmission	63
Gas Distribution	159
Oil Gathering	13
Oil Transmission	28
Petroleum Product Transmission	31
Petroleum Product Distribution	1
Water	28
Total	373

- Gas Gathering
- Gas Storage Area Gathering
- Gas Transmission
- Gas Distribution
- Oil Gathering
- Oil Transmission
- Petroleum Product Transmission
- Petroleum Product Distribution
- Water

These reports are on file at OPS-DOT. Except for the expected differences related. to the materials transported, there were no significant variations in the numerical responses of the separate reports listed above. Therefore, the numerical results of the questionnaire contained in this report are the combined results of the 373 operating companies. The occasional differences in response of gas, oil, water, gathering, transmission, or distribution companies are noted.

All of the responses to each particular essay question were placed together. This permitted a rapid overview of the responses to each question. Where applicable, the results of the essay questions were placed in tables for easy analysis. Many of these tables appear in this report. Other interesting comments were also included and are referenced by questionnaire number, e.g., (Q100). The combined essay questions and the questionnaire responses are on file at OPS-DOT.

The 404 responses represent the experience and knowledge of corrosion control associated with 1,369,947 miles of pipe.

4. Personal Contacts

More than 96 corrosion scientists and engineers from all over the United States were interviewed for both fact and opinion. Local and national meetings of NACE, Electrochemical Society, and the Metallurgical Society of AIME were attended.

5. Outline of Report

The results of the literature survey, the questionnaire, and the personal interviews were combined insofar as possible. The state of the art of corrosion of ferrous piping is summarized and conclusions are given in Section II. Hence, an overview of this study can be obtained. by reading Section I and Section 11.

Current knowledge of the basic forms of corrosion is outlined in Section III. This starts with the basic submerged corrosion mechanisms, which lays the groundwork and explains the nomenclature for understanding the various forms and complexities of corrosion. The forms of corrosion (uniform, pitting, stray current, crevice, etc.) are then discussed in some detail. Next, corrosion control is discussed in Section IV. This includes material selection, inhibitors, coatings, and cathodic protection. This and the following sections are more application oriented and should be understandable to the beginning corrosion student.

Section V presents data on construction, maintenance, and inspection from the questionnaire and the literature. The small amount of published information found on economics is discussed in Section VI. Secticn VII summarizes other problems directly related to corrosion. These include the training of corrosion personnel, the use of piping as an electrical ground, mechanical damage to coatings, and interference. Gaps in the technology and the conclusions are listed in Section VIII.

Appendices I through IV, respectively, present an abstract retrieval run, the questionnaire, a list of electrolysis or corrosion interference committees, and: a list of organizations and societies with interest in corrosion and corrosion control.

SECTION II

SUMMARY

1. Factors Influencing Corrosion

Under normal conditions, metallic iron is unstable with respect to formation of its compounds. Thus ferrous metals corrode underground, in the atmosphere, and in natural waters. This does not necessarily mean, however, that all corrosion is intolerably destructive. It is possible for corrosion to take place at such a slow rate that leaks never develop over the useful life of a pipe section.

Real soil and real engineering metals are not homogeneous. If they were, corrosion would generally be uniform and negligibly slow. In real situations, inhomogeneities exist and cause differences in electrical potential to develop along the surface of a pipe.

Iron dissolves at anodic areas and liberates electrons, which flow through the pipe and participate in cathodic reactions elsewhere. Such galvanic cells arise particularly when different metals are in contact. For example, new steel pipe is anodic with respect to old rusted pipe and dissolves preferentially. Contact with a noble metal such as copper causes steel to corrode rapidly. Galvanic concentration cells may also arise from variations in acidity, oxygen concentration, bacterial activity, etc., along a pipe trench.

Seventy-six percent of the companies surveyed rated galvanic cells as the most prevalent cause of corrosion leaks.

Steel pipe seldom fails by uniform corrosion. It fails predominantly by localized attack in the form of pits. The pits are initiated by some sort of inhomogeneity, as discussed above. Chloride ion seems to be particularly implicated as a causative agent for pitting, as well as for crevice corrosion. Once initiated, a pit rapidly evolves to a fairly stable configuration. Within the pit, iron dissolves to form ferrous ions, which migrate away and react with oxygen and water to form various hydrated oxides in the form of a solid crust. Cathodic reactions, such as reduction of oxygen gas to hydroxide ion or reduction of hydrogen ion to hydrogen gas, occur elsewhere on the pipe. The rusty scale limits access of oxygen to the pit, while negative ions such as chloride are attracted by the large number of positive ferrous ions liberated. Such conditions are conducive for further dissolution, and so the pit continues its self-stimulated but controlled growth.

The surveyed companies believe stray current is their second most prevalent cause of corrosion. Current flows through a pipeline when in an electric field which is present in the soil. Metal dissolves rapidly where positive current leaves the pipe. Electric railways are still a major source of direct current in the soil. Alternating current in power lines induces current in a parallel pipeline and, when rectified, causes Corrosion. Cathodic protection of nearby underground strcctures car. cause current interference. Many measures can be taken to reduce this interference problem, but there are still instances when the high density and arrangement of underground metal structures make avoidance of interference nearly impcssible.

A major threat may be the use of high voltage, direct current power transmission. It is likely that very large currents will at least occasionally be released into the soil. Research is under way to determine the magnitude of the hazard to pipelines and measures which can be taken to reduce corrosion from this source. The effects can be appreciable and may, in some cases, require use of automatic cathodic protection systems.

When high strength steels are subjected simultaneously to mechanical stress and to a corrosive environment, cracks can develop very rapidly. The survey did not show that this is a major cause of corrosion, but it is significant in that failure is apt to be catastrophic. The various stress corrosion cracking mechanisms and phenomena are not well understood and are under active investigation. At this time the only reasonably sure method for preventing stress corrosion cracking is to avoid use of high strength steels. Hard welds should also be avoided for this reason.

Twenty-two leaks were attributed to hydrogen blistering by the surveyed companies. Hydrogen is generated both by corrosion in an acid environment and by cathodic protection, especially at high potentials. Metals with voids and inclusions are particularly susceptible. Intergranular corrosion of many stainless steels can be rapid when the thermal cycle of welding generates certain types of inhomogeneities.

Temperature influences corrosion in several ways; the net effect is generally for corrosion to accelerate as temperatrre increases. Also, stress corrosion crackiny has bee? found to be more common in pipe leading from compressor stations, presumably because of the elevated gas temperatures generated by compression. Corrosion of steel buried in permafrost soils, on the other hand, has been found to be negligible.

Uniform corrosion tends to decrease with time because of the presence of corrosion products blocking access of corrodents. Pitting and stress cracking, however, increase with time. The corrosion failure rate of unprotected pipelines tends to increase exponentially with time.

In general, the most corrosive soils contain large concentrations of soluble salts and, consequently, have relatively low resistivities. On the other hand, the least corrosive soils usually have high resistivities, indicating low concentrations of soluble salts. Soils with resistivities greater than about 5,000 ohm-cm can generally be expected to be mildly to noncorrosive. It should be realized, however, that because many other factors may affect the corrosion rate of metal, certain high resistivity soils may be more corrosive than soils of lower resistivity.

The pitting rate of metal buried in soil has been found to increase exponentially as a function of soil aeration. The lower the amount of aeration, the faster the pitting rate increased with time.

Chloride ion is known to accelerate corrosion. Hydrogen sulfide accelerates corrosion, and can cause sulfide stress cracking. Carbon dioxide pressures over 30 psi in wet oil and gas cause corrosion. The splash and tidal zones in seawater are the most corrosive marine environment. Furthermore, cathodic protection is ineffective there.

It is known that products of microbiological metabolism can accelerate corrosion. Sulfate reducing bacteria cause H_2S formation under anaerobic conditions and accelerate corrosion. The extent to which micro-organisms contribute to pipeline corrosion is uncertain. Very little good field data are available. There tends to be a significant polarization of opinion on this subject.

In the atmosphere, corrosion is accelerated by moisture, wind-blown sea salt, sulfur dioxide, and to some extent, ozone. The combined effect of dilute sulfuric acid and ozone is worse than the sum of their individual effects.

2. Corrosion Control

It is rarely feasible to completely eliminate all corrosion in practical situations. The goal is rather to bring corrosion to an acceptable level for the lowest cost. Nearly all of the companies surveyed had a corrosion control program.

Although no ferrous metal is untouched by corrosion, the extent of corrosion is significantly influenced by the exact composition of the metal and by thermal and mechanical treatments. Welds are noted to be particularly susceptible to corrosion. Unfortunately, most of the additives which markedly improve corrosion resistance are probably too expensive for use in large pipeline systems.

Although most corrosion occurs externally, internal corrosion is also a problem when moisture and chloride ion, hydrogen sulfide, or carbon dioxide are present. This has been controlled by removing moisture (drying the gas and oil streams), adding inhibitors, or coating. Proper inhibitors are selected empirically. It is important to note that many inhibitors accelerate corrosion if their concentration is too low.

A widely used method of corrosion control is the application of coatings. Although metal coatings are effective under some conditions, thick organic coatings are generally favored for underground use where protection is required for long periods. These coatings are ideally water impervious, electrically insulating, and tough. Generally, tight adhesion to the pipe is also required, although good results have been reported with loose fitting plastic sheaths. The requiremeet for water impermeability is probably even more severe when the coating is not bonded to the pipe. It should be noted that no perfect coating material exists.

The most common circumstance for leaks in coated. pipe was physical damage of the coating. The second most common circumstance was corrosion at improperly applied coatings. Microorganisms attack most, if not all, organic coatings. Therefore, one cannot assume that once a pipe is coated it remains effectively coated forever. Inspection and repair is necessary not only when laying pip, but also periodically thereafter. The maintenance requirements are probably particularly severe when cathodic protection is not employed simultaneously.

Although seldom used for pipes carrying gas and oil, concrete coatings can provide effective corrosion control. Concrete's effectiveness is largely due to its high pH. Again, proper application is required, including choosing the proper concrete mix.

In cathodic protection, corrosion is reduce2 by making the pipe negative with respect to the adjacent soil. It is not a panacea for all corrosion problems. Neither is the proper application of cathodic protection a trivial matter. Increased corrosion due to cathodic protection has actually been observed when steel was continuously or intermittently heated and intermittently wetted. Such conditions would be expected on pipes just downstream from compressor stations in areas where the soil is intermittently dry and wet. Cathodic protection can increase the leak rate at first, when applied to old pipe, by loosening the adherent rust scale which previously covered small holes. Cathodic protection may be accomplished either by externally applied DC power or by attachment of sacrificial anodes, such as Mg, Zn, or Al, which are slowly consumed. Either method is effective when properly installed and maintained.

It may be possible to maintain coatings to the extent that adequate protection is achieved without other measures. However, the difficulty in achieving this level of maintenance has caused many conpanies to supplement coatings with cathodic protection. On the other hand, cathodic protection used alone can generally provide adequate protection, except that large currents are required and interference with other structures that may be nearby is likely. When used with coatings, only enough current is required to protect areas where holes have developed in the coatings. Thus, coatings and cathodic protection are often used in conjunction. Even though the data from the surveyed companies indicated a lower corrosion leak rate with coated and cathodically protected pipe than with unprotected pipe, some leaks did develop on protected pipes. Thus the control measures do not appear to be totally effective. In many cases, this may reflect improper use of either coatings or cathodic protection, or both.

Use of cathodic protection and coatings together is not without problems. Cathodic protection may cause disbonding of the coating. Cavities under disbonded coating are ideal for crevice corrosion and microbiological corrosion. To a large extent, cathodic protection is ineffective in disbonded areas. Cathodic protection increases the pH in the surrounding electrolyte, which damages many coating materials.

Cathodic protection has been found to cause calcium carbonate and magnesium hydroxide deposits to form on steel in salt water. These not only help protect the metal, but gradually reduce the cathodic protection current as well. The best coatings were found to be formed at lower current densities (< 150 mA/sq ft) and to consist primarily of calcium carbonate. One can cause similar deposits to form on buried pipe by adding calcium bicarbonate to the backfill and applying cathodic protection.

There appears to be no entirely satisfactory criterion for verifying that cathodic protection has been achieved. Potentials cannot be made too negative or coatings are disbonded. Most of the companies surveyed used a pipe potential of 0.85 volt relative to the copper sulfate electrode as their criterion for cathodic protection. The second most common criterion used was a 300-mV difference between the energized and the original open circuit potentials. Most of the companies surveyed used more than one cathodic protection criterion.

Pipelines passing under roadways are frequently encased in outside metal casings. There is evidence to the effect that such casings are unnecessary for structural safety. Furthermore, when the metal casing becomes shorted to the pipe, cathodic protection is ineffective. The companies surveyed had a total of 22,669 casings shorted to the carrier pipe, Over 300 leaks were reported inside casings for 1969.

3. Construction, Inspection, and Maintenance

To ensure good corrosion control, one must not only design the control systems properly, but also draw up detailed specifications, inspect the work, and periodically maintain the system. Sixty-one percent of the surveyed companies used clamps to repair at least some of their leaks, while 54 percent replaced portions of the pipe. The main criterion for replacing pipe was the leak history. The most common annual surveillance method was a pipe-to-soil potential survey, while the second most common was line current measurement. The 373 operating companies reported 252,552 corrosion leaks during 1969 for 1,369,947 miles of pipe.

SECTION III

FORMS OF CORROSION

Two hundred and fifty-three of the surveyed operating companies indicated in the questionnaire that they determine the probable type of corrosion with regard to corrosion leaks. Table 3 summarizes opinions as to the most prevalent causes in each company.

MOST PREVALENT

	1st	2nd	3rd	4th	5th	6th	7th	8th
	Number of Companies							
(A) Galvanic Cell	284*	18	?	0	0	0	0	0
(B) Stray Current (including cathodic interference)	19	150	41	4	0	2	0	0
(C) Stress Corrosion Cracking	3	17	21	15	4	1	0	0
(D) Corrosion Fatigue	4	13	17	4	3	0	0	1
(E) Hydrogen Embrittlement	2	0	3	3	2	2	4	1
(F) Caustic Embrittlement	0	3	3	1	2	4	1	2
(G) Microbiological Corrosion	7	32	33	10	4	0	2	0
(H) Other	11	9	10	2	0	0	0	0

*Unless otherwise specified, the numbers contained in the tables are the number of operating companies out of the total 373 companies that responded to that particular question in the questionnaire.

Galvanic cell corrosion was the most prevalent cause according to 284 companies. Stray current was the second most prevalent cause for 150 companies. For 19 companies stray current was the major problem. Microbiological metabolism was apparently a significant cause for corrosion for 30 percent of the companies polled. Many companies apparently felt that stress corrosion cracking and corrosion fatigue were a prevalent cause, but only a few leaks due to stress corrosion cracking and corrosion fatigue have been reported.

Table 4 gives the supplemental measurements that companies have used to identify causes of corrosion leaks.

TABLE 4

MEASUREMENTS THAT HAVE BEEN USED FOR IDENTIFICATION OF CAUSES OF CORROSION LEAKS

	Number of Companies
(A) Coating Thickness	137
(B) Chemical Analysis of Soil	47
(C) Pipe Potential	275
(D) Maximum Pit Depths at Adjacent Corroded Areas Within the Excavation	187
(E) Metallurgical Analysis	46
(F) Redox Potential	9
(G) Soil pH	88
(H) Soil Resistivity	230
(I) Qualitative Field Test for Sulfide Ion	5c
(J) Potential or Current with Respect to Foreign Structure	219

There are two compelling reasons for studying the underground corrosion processes. These are: (1) To define the conditions and constituents in the soil which contribute to the soil's corrosiveness, and (2) To define the reactions at and near the metal surface so as to provide a theoretical basis for cathodic protection criteria to supplant the empirical methods in present use.

Definition of the soil conditions which contribute to corrosiveness would make the soil corrosivity survey more positive in results and of great economic value to industry. However, only a few of the operating companies in the United States strive for this objective as shown by Table 4.

Many operators rely upon soil resistivity as a measure of the soil's corrosiveness. This indicator is inadequate to completely define corrosivity. A neutral carbonate soil would be relatively innocuous compared to one containing soluble chlorides and sulfates at the same resistivity. Many similar comparisons can be made where resistivity alone is seen to be insufficient information for predicting corrosivity.

The pipe potential (Part C of Table 4), including that with respect to neighboring pipelines (Part J of Table 4), is used extensively to find the cause of corrosion leaks. The magnitude of a steady potential can often detect lack of cathodic protection, overprotection, galvanic activity and cathodic interference, Fluctuating currents are helpful in discovering the source of interference current.

1. Basic Corrosion Mechanisms

Corrosion is an electrochemical process with an anodic reaction as

$$\mathrm{Fe} \rightleftarrows \mathrm{Fe}^{2+} + 2\mathrm{e}- \qquad \text{(Eq.1)}$$

and such cathodic reactions as

$$2\mathrm{H}^{+} + 2\mathrm{e}- \rightleftarrows \mathrm{H}_2, \text{ or} \qquad \text{(Eq. 2)}$$

$$\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} + 4\mathrm{e}^{-} \rightleftarrows 4\mathrm{OH}^{-} \qquad \text{(Eq. 3)}$$

Once formed, the Fe^{2+} is not normally stable, but reacts with oxygen and water to form magnetite, Fe_3O_4, or hematite, $Fe_2O_3 \cdot 3H_2$. This latter compound, both dehydrated and variously hydrated, is called rust. The equilibrium existing between iron and its corrosion products may be found by thermodynamic calculations. The results are presented in the form of phase diagrams, often referred to in corrosion theory as Pourbaix plots.

It is generally thought that certain regions on a given piece of steel are anodes while other parts are cathodes. These regions may be microscopically near one another or very far apart. Microelectrode experiments have confirmed that some regions are primarily anodic and others are cathodic (779).

In recent years, much attention has been devoted to uncovering the reaction mechanisms at the electrodes, since the above reactions are merely what is externally observed and tell nothing about the various steps involved (758, 760, 761, 766-768). Even without this detailed knowledge, however, one can profitably make use of the concepts of electrode kinetics. In corrosion this takes the form of mixed potential theory (763). Consider the reaction of Equation 1 taking place at an electrode. Electrons are being liberated at the metal surface while positive ionic current flows into the electrolyte. As the electrode is made more positive, the reaction rate increases as shown in Figure 1. Soon, however, iron passivates and the reaction rate decreases. Very high potentials again cause the current to increase. Passivation results from the formation of a solid film at the metal surface which interferes with ion and electron flow.

On the other hand, the iron can also serve as an electrode for a cathodic reaction, such as Equation 3. For this reaction, the rate increases as the surface is made more negative. If, as is usual, the metal surface has both anodic and cathodic regions, then both reactions proceed simultaneously. If no external source or sink of electrons is available, then the rate of both reactions must be equal at the point where the curves in Figure 1 cross. The linear corrosion rate, R, is related to this intersection by

$$R = \frac{i_{corr} V_m}{nFA} \qquad \text{(Eq. 4)}$$

where i_{corr} is the corrosion current, (given by the intersection of curves in Figure 1), V_m is the molar volume of the metal, n is the number of electrons exchanged in the anodic corrosion reaction (two in Equation 1), F is Faraday's constant and A is the surface area of the metal. In the case of several simultaneous anodic reactions, the I-E curves for each are added and the system again operates at the intersection of the curves.

The origins of the anodic and cathodic curves are the points at which forward and reverse reactions are taking place at equal velocities i.e., equilibrium for that particular reaction. The

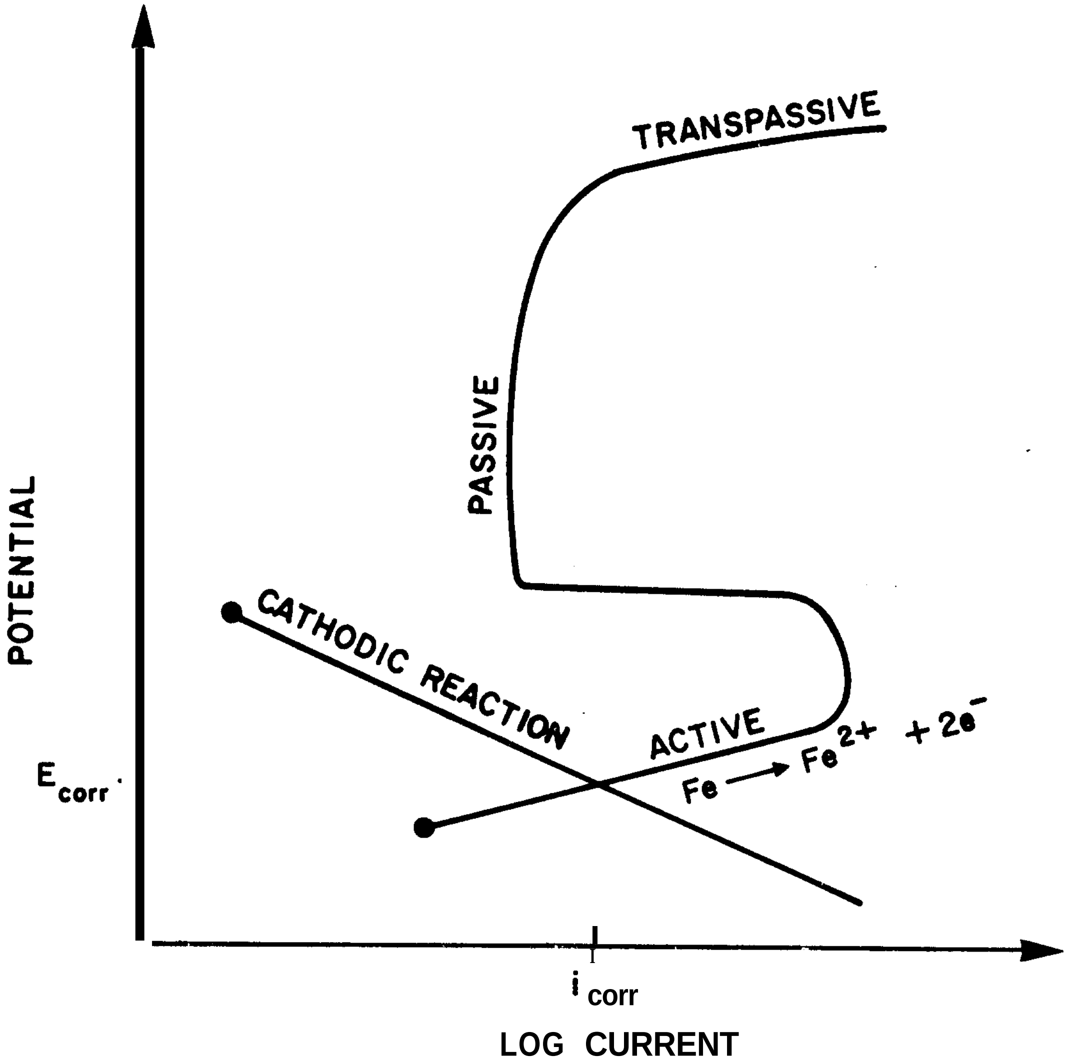

Figure 1. Mixed Potential Diagram for Corrosion of Iron (Schematic)

potentials at those points are given by the half-cell potential, which, using Equation 3 as an example, may be given by the familiar Nernst Equation of chemical thermodynamics,

$$E = E^{o} - \frac{RT}{nF} \ln \left(\frac{a_{OH^-}^{4}}{a_{O_2}} \right) \qquad \text{(Eq. 5)}$$

where E^O is the standard half-cell potential for unit activities of reactants and products, R is the gas constant, T is absolute temperature, n is the number of electrons in the reaction (four for this example), F is Faraday's constant, and the a's are activities, which equal concentrations for ideal mixtures. Note the concentration of reactants influences the potential at the origins.

The mixed potential theory is not only useful conceptually, but also provides the basis for instantaneously measuring corrosion rates and studying electrode reaction mechanisms. An external potential is applied and the current measured. The current observed will actually be the difference between the two curves of Figure 1 at some specified potential. Thus, potential and current measurements of the system shown in Figure 1 would yield the cathodic polarization curve of Figure 2 and the anodic polarization curve of Figure 3.

Kinetic studies have shown that several steps are involved in net cathodic and net anodic reactions, Theoretically, when one step controls the rate of an electrode process, the kinetics follow the Tafel equation (766, 768),

$$\eta = \alpha \pm \beta \ln i \qquad \text{(Eq. 6)}$$

where η is the overpotential (deviation of potential from the reversible value), α is the value of η at current $i = 1$, and β is the "beta constant," "Tafel constant," or "Tafel slope." This equation implies a straight line on semilogarithmic plots as in portions of the curves of Figure 1. Measurements of β and the effects of varying solute concentrations permit deductions about mechanisms of reactions at electrodes.

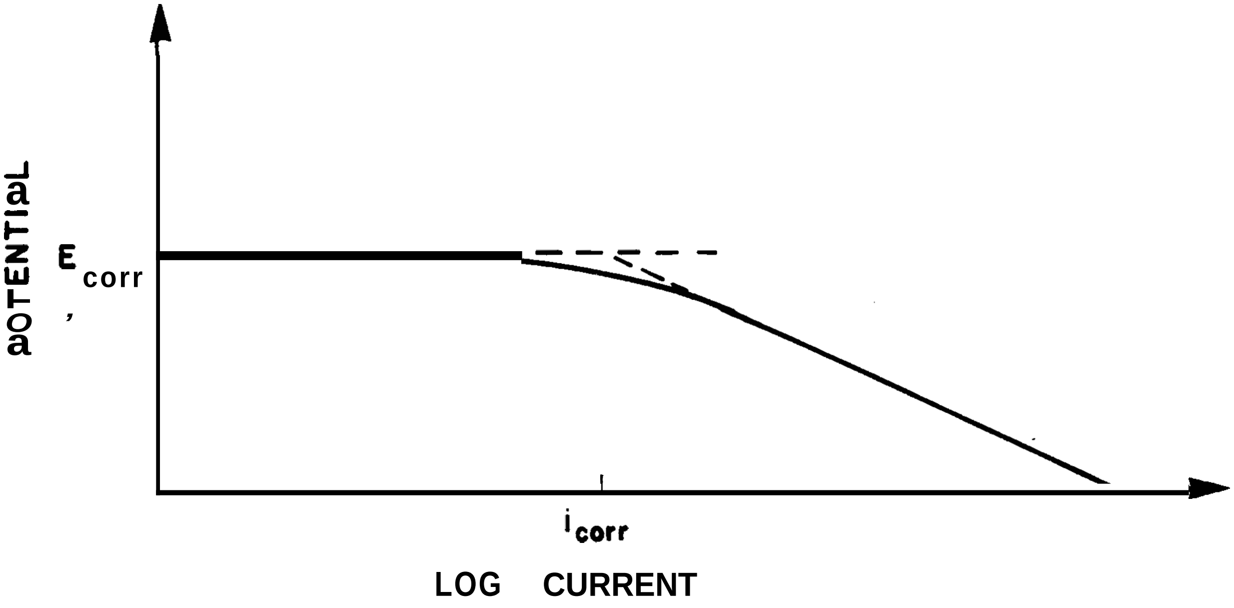

Figure 2. Cathodic Polarization Curve

Corrosion engineering and science now utilize a wide variety of experimental techniques in addition to polarization studies. These range from simple pit depth, loss in weight, and thickness measurements to very sophisticated methods such as ellipsometry, electron diffraction, radiotracers, and the use of the electron microscope (688).

2. Internal and External Pipeline Corrosion

The basic mechanisms for corrosion are the same for internal and external corrosion, although the environments are quite different. In most instances, the exterior environment is much more corrosive than the interior, which is fortunate because corrosion mitigation is much simpler on the outside.

Roughly 75 percent of the gas transmission lines in the United States were surveyed during the period from 1 July 1967 to 30 June

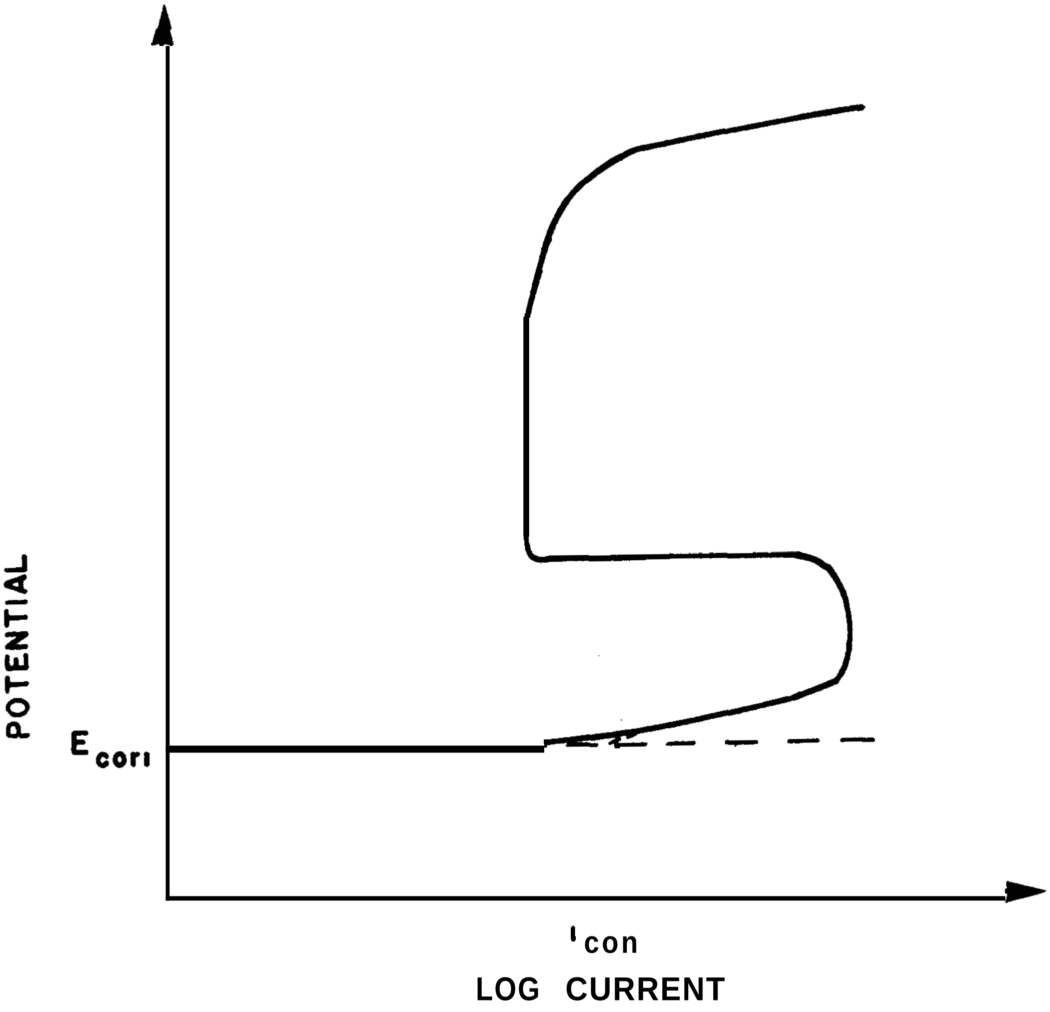

Figure 3. Anodic Polarization Curve.

1968 to determine causes of pipeline failures; the survey covered both preservice tests and inservice operational failures (586). The primary cause of test failures was the longitudinal weld, whereas external damage (bulldozer, ditcher, etc.) was the prime cause in operational failures, with corrosion and the longitudinal weld as the next most frequent causes. A number of failures in older, uncoated lines or poorly coated lines were found to have occurred as a result of external corrosion. In these failures, the wall thickness is gradually reduced to the point at which failure results. Hydrogen cracking in hard spots in the pipe wall were found to have caused failures after the pipe had been in service for 2 to 15 years. Hard spots are localized hard regions, usually with hardnesses in the range of Rockwell C 39 to 51, that have ranged from about 2 to 10 inches in diameter in the base metal. Stress-corrosion cracks in most instances were found in areas that were essentially free from both pitting corrosion and general corrosion. A few failures from hydrogen blisters were found in gathering lines containing sour gas. Failure can occur from formation of a blister on either the inside or outside surface of the pipe resulting from generation of atomic hydrogen in the attack of the steel by the H_2S and moisture in the sour gas. Longitudinal weld failures in service pipe were found to have resulted frcm selective corrcsion and hydrogen cracks in hard regions.

Table 5 indicates the most prevalent circumstances under which corrosion leaks of coated pipe have been found by the 373 operating companies during the last five years. As may be seen, the most prevalent causes of leaks are at locations of external damage and improperly applied coating, irregardless of whether the pipe is cathodically protected or not.

Table 6 lists the number of leaks in 1969 that occurred at joints and welds. For example, eight companies had one cr two compression coupling leaks whereas 20 companies had over 15 leaks. The companies with over 15 leaks generally had a deficient piping system with many leaks at the joints. With the exception of a

TABLE 5

MOST PREVALENT CIRCUMSTANCES UNDER WHICH CORROSION LEAKS OF COATED PIPE HAVE BEEN FOUND DURING THE LAST 5 YEARS

	Order of Frequency					
Cathodically Protected	1st	2nd	3rd	4th	5th	6th
	Number of Companies					
(A) Corrosion at Improperly Applied Coating	55	56	20	4	4	1
(B) Corrosion Where Coating Has Clearly Been Damaged During Construction or Subsequently Abraded by Others	81	35	15	5	5	0
(C) Corrosion Where Coating Is Ruptured by Soil Stress or Root Growth	4	22	23	15	13	2
(D) Corrosion Beneath Unbonded Coating	13	22	28	16	6	1
(E) Failure of the Coating Material	12	13	13	11	12	1

Not Cathodically Protected	1st	2nd	3rd	4th	5th	6th
	Number of Companies					
(A) Corrosion at Improperly Applied Coating	43	65	28	6	2	1
(B) Corrosion Where Coating Has Clearly Been Damaged During Construction or Subsequently Abraded by Others	108	42	17	2	0	0
(C) corrosion Where Coating Is Ruptured by Soil Stress or Root Growth	8	19	18	21	15	1
(D) Corrosion Beneath Unbonded Coating	5	10	36	23	11	1
(E) Failure of the Coating Material	11	18	15	12	11	1

TABLE 6

NUMBER OF CORROSION LEAKS OCCURRING IN 1969 AT JOINTS AND WELDS

JOINTS

	Number of Leaks				
	1-2	3-4	5-6	7-15	over 15
(A) Compression Couplings	8	6	12	11	20
(B) Threaded Couplings & Flanged Joints	19	11	3	26	33
(C) Other	5	4	2	3	15

WELDS

	Number of Leaks				
					over 4
(A) Longitudinal Factory Welds	8	4	4	2	12
(B) Spiral Factory Welds	0	0	0	0	2
(C) Field Welds	6	9	3	0	27

few existing piping systems, the leaks at. joints and welds are insignificant when compared to the total number of leaks.

3. Uniform Corrosion

Uniform removal of metal is the least troublesome of the various forms of corrosion. However, it is the easiest form of corrosion to study, and as a result much of our fundamental knowledge of corrosion comes from research on uniform corrosion processes. For example, the uniform corrosion rate is what one determines directly from polarization studies (7, 537). Errors can arise, however, if another anodic reaction is of comparable magnitude to the metal removal reaction. This has arisen, for example, from the oxidation of hydrogen under pressure (hydrogen exchange! during corrosion in a sealed autoclave (547). Corrosion current was 9.8 times the actual corrosion rate. Cathodic polarization studies of iron in one normal halogen acid showed the hydrogen coverage to be near one monolayer at the corrosion potential (153). This seems to indicate that nearly the entire iron surface functions as a cathode during corrosion and that only a small part of the surface undergoes dissolution at any given time. Radiotracer studies of iron in water revealed that no corrosion takes place if oxygen is excluded and that negligible exchange of iron atoms with the solution takes place (265).

After a film was formed on iron in water containing oxygen, the Tafel portion of the polarization curve was found to change in slope (β decreased) as the film thickness increased (235). For thin films it was concluded that the charge passed was used in the formation of iron-ion vacancy-electron pairs and for transfer of oxygen from the solution to the outer layer of the oxide. The field drives ions through the layer **(478).** In the transient state there is a nonzero charge distribution in the layer which slowly decays when steady state current is restored. (This may be related to the effect of AC on corrosion.) It has been suqgested that the film continuously dissolves and so must be regenerated to maintain passivity (692). The effects of complexing agents, potentials, inhibitors, and double layer on corrosion were explained by their influence on dissolution of the film.

4. Pitting

Steel pipe generally does not fail by uniform corrosion. It fails predominately by localized attack in the form of pits. Pits appear to be initiated when local penetration of the surface film occurs on steel generally protected by the film. That is, it is a form of attack intermediate between general attack and complete passivation. When the fluid in a pipe is under pressure, a pipe may possibly fail by fracture before the pit completely penetrates the wall (598).

Most pitting appears to be associated with chloride ions. Bromide and hypochlorites cause pitting, while fluorides and iodides have little effect. Cathodic reactions occur on the surface of the steel, while anodic dissolution takes place in the pit. Thus, an excess of positive charge is produced in the pit, which attracts the negative chloride ions (769). It has been claimed that pitting is more severe on the top side of pipe than on the bottom because the solution in the pits is heavier than the surrounding electrolyte (769); however, analyses of extensive field experience on buried pipelines have shown that pits occur more often on the bottom of pipes. This is attributable to several factors -- a higher salt concentretion and moisture content at the bottom because of drainage and because the soil is packed more tightly there, and a lower oxygen concentration because of the greater distance from the soil surface. This offers one explanation for pit initiation on polycrystalline steel surfaces. Commonly, pits appear to be preferential in location and direction, probably following veins of high impurity content introduced during casting, rolling, etc. Since pitting is a statistical phenomenon, the maximum pit depth increases as the surface ares of the sample increases, often being proportional to the 0.15 power of the area (687).

It has been found in polarization studies that when potentials on passive surfaces are lowered, a point is reached where the current rapidly increases. This has been interpreted as due to initiation and autocatalytic growth of pits. The breakdown potential has been called the "critical" or "pitting" potential, with the suggestion that pitting does not occur at more active (negative) potentials. Thus, measurements of pitting potential have been employed to compare pitting tendencies of metals and electrolytes (e.g., 154, 772, 285). However, this procedure, and in fact the whole concept, has recently been severely criticized. In one paper it was concluded that pitting potential is related to pitting, but questioned that it is a basic characteristic of the alloy (770). It was found that the rate of potentiodynamic scanning and time of holding during potectiostatic polarization have a marked effect on the measured value of critical potential. It has been found that the rates and types of corrosion of stainless steel in chloride media were quite different for controlled potential corrosion tests than with conventional corrosion tests under identical conditions of concentration, temperature, and potentia?. (771). The electrochemical tests more often produced pitting. These results were attributed to the migration and surface accumulation of Cl^- during potential measurements.

Considerable evidence has been accumulated to show that chloride ion causes breakdown of the passive film. In polarization studies with Cl^- added to a solution contacting passive iron, it was found that an induction period is necessary before the anodic current increases (773). The induction period was inversely proportional to the Cl^- concentration, with a minimum concentration required for attack (328). A freshly passivated surface was less resistant to Cl^- than one at steady state. These results have been explained by migration of Cl^- through the film. A second induction period has also been observed, beyond which porous $\gamma\text{-}Fe_2O_3 \cdot H_2O$ grows on the surface, allowing easy local dissolution leading to pitting (773).

Once initiated a pit rapidly develops into the configuration diagrammed in Figure 4. All of the factors influencing the progress and development of a pit during underground corrosion could not conveniently be included in a single diagram. However, this diagram, supplemented by Table 7, suffices for description of the more evident characteristics.

Thus referring to Figure 4:

(1) The liquid-gas interface shown at the top ranges from the liquid boundary of a partially or fully submerged pipeline to the thin film of moisture either on the pipe surface or bridging a soil particle and the pipe. The availability of gases at the pipe may be severely limited in the first case, whereas in an open textured soil the gas may be abundantly available through. a thin moisture film and is quickly replaced if consumed.

(2) Four gases are shown in equilibrium with the liquid phase. Oxygen and hydrogen sulfide are soluble in water, while carbon dioxide and ammonia react with water to form new ionic species:

(a) Oxygen., comprising one-fifth of the earth's atmosphere, is well dispersed in open textured soil; it is also produced by

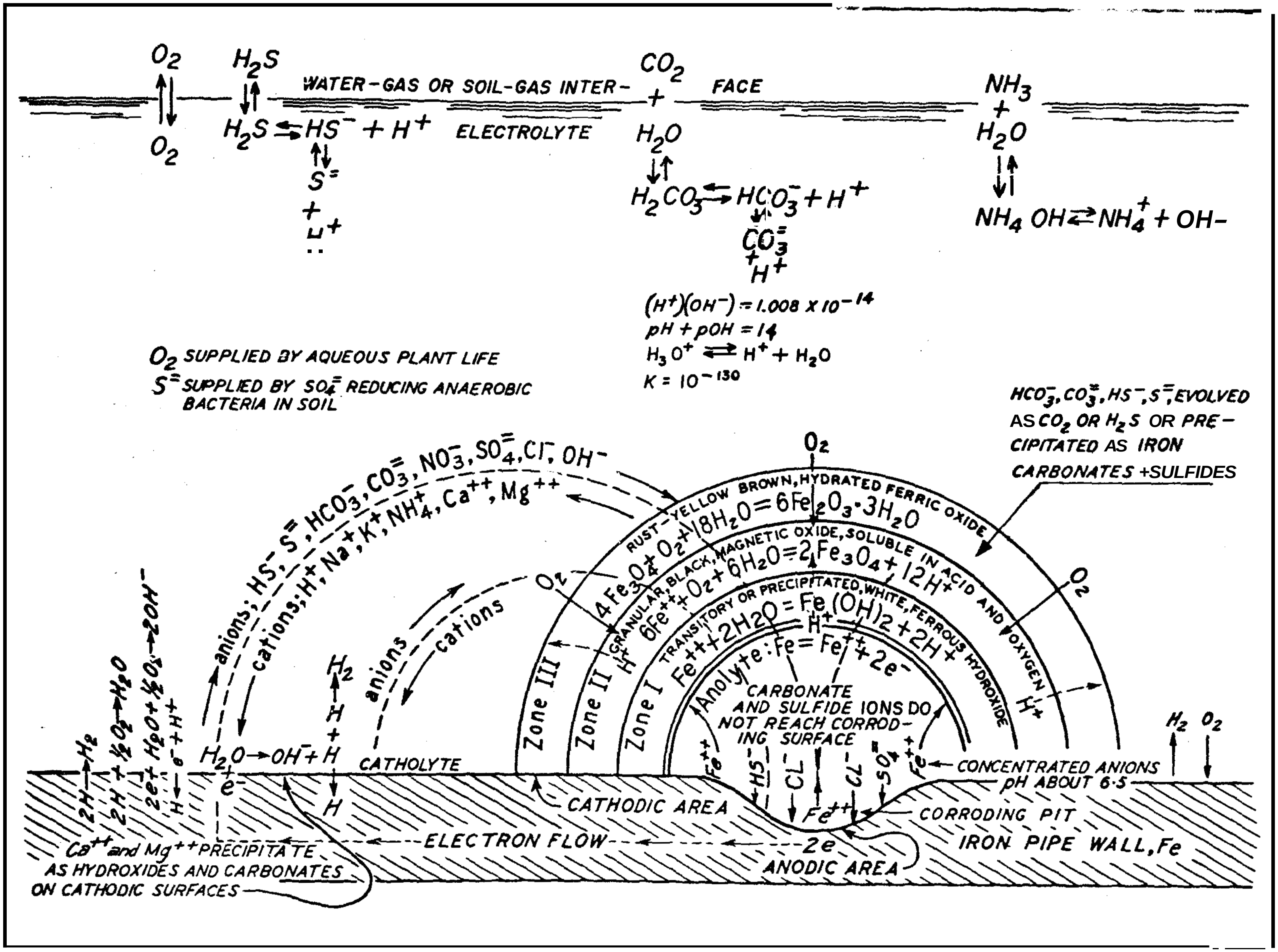

Figure 4. Schematic Representation **of** the Underground Corrosion' **Process**

TABLE 7

SOME OXIDES, SULFIDES, AND SALTS OF IRON APPEARING IN CORROSION PRODUCTS

Substance	Formula	Solubility	Color, Form
Ferrous hydroxide	$Fe(OH)_2$; $FeO \cdot H_2O$ (a)	(1) (2) (5)	White, crystalline
Ferric hydroxide	$Fe_2O_3 \cdot 3H_2O$; $Fe(OH)_3$ (b)	(1) (2) (5)	Red-yellow to brown
Ferrosoferric oxide	Fe_3O_4; $Fe_2O_3 \cdot FeO$ (c)	(1) (3)	Black, granular
Ferrous sulfide	FeS	(1)	Black to brown
Ferric sulfide	Fe_2S_3	(1)	Yellow-green
Ferrous chloride	$FeCl_2 \cdot 4H_2O$ (d)	(4)	Blue-green
Ferrous sulfate	$FeSO_4 \cdot 7H_2O$ (d)	(4)	Blue-green

(a) Not normally written as the hydrated oxide since FeO is black
(b) Rarely written as the hydroxide
(c) The oxide is magnetic and has an affinity for water, i.e., $Fe_3O_4 \cdot H_2O$
(d) These salts precipitate with fixed proportions of water

(1) Highly insoluble
(2) Soluble in acid
(3) Soluble in acid in the presence of oxygen
(4) Highly soluble
(5) Soluble in alkali

plant life which may cause the concentration in soil moisture to read- values well above the normal 9 to 10 parts per million. The oxygen concentration is probably near the equilibrium value at almost every point in backfilled soil.

(b) Hydrogen sulfide is an end product of the reduction of sulfate ion by anaerobic bacteria and is, unlike oxygen, produced in soil and often at the pipe surface,

(c) Carbon dioxide, important in the life cycle, reacts with water to form the diprotic acid which dissociates as shown. It is of either atmospheric or biological origin. It is an initiating factor.

(d) Ammonia, frequently introduced into the soil as a fertilizer, reacts with water to form ammonium and hydroxide ions.

(3) The product of the concentrations of the components of dissociated water and the consequent relation between the pH and pOH are appropriately shown in the central portion of the diagram. The hydration of hydrogen ions and the equilibrium constant are also shown there. (The unhydrated proton, H^+, is evidently non-existent. However, it is used in the figure for simplicity. It is to be read as the hydronium ion, H_3O^+.)

(4) A pit is shown in the pipe wall at the bottom of the page along with the uncorroded area to the left, in order to illustrate the well established electrochemical theory of corrosion. In the ideal case a large cathodic area is concentric with the anodic pit where iron goes into solution and gives electrons to the metal. These electrons move to the cathodic areas where they participate in a reduction process such as illustrated by Equations 2 and 3. The iron atom cannot go into solution carrying two positive charges without negatively charged ions being available to balance the charge. Either one doubly charged anion such as sulfate or a pair of single charged ions such as OH–, Cl^-, or HS^- must be provided. If the electrolyte at the point of corrosion is alkaline, ferrous hydroxide precipitates.

As corrosion proceeds, the anions move through the electrolyte (soil, water) along an arc toward the anode, while the cations follow similar paths to the cathode. The larger arc shows the direction of flow of the ions usually found in soil. The solution through which soluble salts are transferred from one area to another under the electric gradient established between anode and cathode is the electrolyte and, logically, the electrolyte at the anode is the anolyte and that at the cathode, the catholyte.

If the transport arcs are imagined to be shortened, to the point that the adjacent reacting surfaces are of atomic dimensions, then the process is referred to as chemical corrosion and a more general attack of the corroding surfaces results.

According to classical theory, the reaction at the anode is confined to the formation of ferrous ion. But there is evidence that other reactions can sometimes occur there. This will be discussed later.

Shown toward the left in the figure are four reduction reactions. Two reactions account for the disposition of the same number of electrons as released at the anode. Two show disposition of monatomic (nascent) hydrogen (a) by evolution of hydrogen gas, and (b) by reaction with oxygen to form water. In electrolytes low in pH the formation of molecular hydrogen is favored. On the other hand, abundant oxygen is known to depolarize cathodes in electrolytes high in pH. A fifth reaction in the figure emphasizes the tendency of the catholyte to increase in pH as corrosion proceeds.

(5) Overlaying the pit are zones of a corrosion product mantle illustrated in the form of a rainbow. The oxidation state of the iron in the oxides increases outwardly from ferrous through ferrosoferric to ferric. The order of appearance of these oxides is invariant. Some properties of the oxides are shown in the diagram and are supplemented in Table 7. Ferrous and ferric hydroxide have each been found alone in the field -- the former under anaerobic conditions and the latter under strongly aerobic exposures. Ferrous hydroxide is found, for example, in wet clays along the banks of "bayous" in Texas. The white oxide changes on exposure to air to the familiar red-brown ferric oxide. Pure white ferrous hydroxide has been observed in pits beneath a bituminous coating on pipe under cathodic protection, which produces a reducing environment. Pure ferric hydroxide has been produced under a high potential in the presence of oxygen and has been observed in the field under similar conditions. All three oxides have been reported in coexistence in nature and all three can easily be produced in "rainbow" order in the laboratory. Magnetite has been found neither alone nor in combination with ferrous hydroxide. The overwhelmingly prevalent combination is magnetic oxide overlain with ferric oxide. Even in dried samples of these oxide scales removed from pipe and iron structures above ground there always remains an underlayer of magnetite. The oxidation never seems complete even upon prolonged exposure to air. Ferrous and ferric oxide have not been observed together without the intermediate oxide.

There are two interesting characteristics of the corrosion product mantle. First, considerable quantities of water are consumed in the precipitation of the oxides. Second, the release of hydrogen ion tends to carry water away from the corroding area due to hydration. Tests on samples of rust taken in the field show that the pH of Zone III is of the order of 3.5, whereas the pH of the anolyte is only slightly acidic, as indicated in the figure.

The orderly flow of anions is interrupted in Zone III by reaction of incoming sulfides and carbonates with hydrogen ions and consequent evolution of hydrogen sulfide and carbon dioxide and neutralization of hydroxide ions. Iron sulfides have not been found in Zone 111. Nitrate ions, generally rare in soil, presumably oxidize the iron oxides to the ferric state. These reactions thus allow only the chloride and sulfate ions, and possibly bisulfide, to reach the anolyte. On the other hand, the orderly flow of cations is uninterrupted to the metal surface, where magnesium and calcium ions precipitate as hydroxides and carbonates. There hydrogen ions, if any, are also neutralized. Sodium and potassium ions accumulate at the surface, and the pH tends to increase.

Two facts of interest in the movement of the ions are: (a) that while the current density in the cathodic area is a maximum near the pit, it attenuates rapidly with increase in the radius of the transport arc; and (b) that diffusion, predominates over the migration of the ions due to the influence of the electric field established by the corrosion processes.

(6) The corrosion product mantle is never as ideally constituted as depicted in the figure. The magnetic oxide fills and overlays the pit in the absence of ferrous hydroxide. It is porous and essentially free of condensed moisture. The participation of water in the formation of the several oxides has been mentioned. Added to this drying effect is the repulsion of hydronium ions by the electric field. However, the voids are saturated with water vapor. In accord with thermodynamic considerations, the anolyte is barely acid and the black oxide may exhibit a greenish cast indicating its saturation with ferrous chloride. Pale green crystals of this salt have been picked from the black granular mass. They develop a thin brownish coat on exposure to air. Water of crystallization further depletes the anolyte of free water.

Chemical analysis of material in pits has been more extensive in pipe coated with cement mortar than with pipe either bare or coated with organic materials. In these analyses the ratio of iron to chlorine is always in good agreement with ferrous chloride stoichiometry. Sulfate and other ions appear in the anolyte in traces only, The mortar reacts with sulfate ion and inhibits its transport to the pit.

(7) The mechanism for the formation of magnetite is obscure. The problematical equations in the mantle are intended primarily to show the end products and to give a reasonable account of their formation in accord with observation. A number of other equations could be written but these would be equally speculative. However, there is evidence that magnetite forms spontaneously from ferrous

hydroxide with evolution of hydrogen. This reaction is used to explain the formation of magnetite in boiler tubes. The reaction is thermodynamically possible. It has been suggested that once formed the ferrosoferric oxide seeds its continued production. On the other hand, mounting evidence shows that under high aeration ferric ion forms directly from the metal. Thus the potential of the Fe,Fe^{3+} couple would favor this reaction in a solution saturated with ferrous chloride combined with a highly aerated cathode provided, of course, that the activity of the ferric ion is maintained essentially at zero by precipitation of the magnetic oxide.

(8) The overall potential of the going cell may be approximated by thermodynamic calculations. The potential of iron in equilibrium with its salts $FeCl_2 \cdot 4H_2O$ and $FeSO_4 \cdot 7H2O$ as required by the schematic, are readily computed (Table 7). The potentials of the hydrogen and oxygen electrodes present problems relating to the absorption of hydrogen by iron and lack of information on the reactions at the electrode surfaces. Further complicating the approximations, the substantial redox potential between Zones II and III must be taken into account. It would appear easy to measure the actual potential in the anolyte and the redox potential in Zone III and the cathode potential in a case approaching the ideal. Some such measurements have been made in the field. The mixed potential taken remotely, as on the surface of the earth over the pipe, is poorly informative except with respect to the order of the reaction on the metal surface. This is generally found to be bifaradaic (two electrons exchanged), in

accord with classical theory. As a practical matter, opportunities for test are few. Excavations are generally made for repair of pipe, and in such cases the corrosion cells are destroyed by escaping oil, gas, or water.

As a matter of interest, it is noted at this point that oxygen may play three roles in the corrosion process, namely, (a) removal of adsorbed and absorbed hydrogen, (b) its direct reduction at the cathode, and (c) its reduction within the mantle to form ferric oxide. Perhaps the reaction

$$4Fe^{2+} + O_2 + 2H_2O = 4Fe^{3+} + 4OH^- \qquad \text{(Eq. 7)}$$

should be included in discussions of basic mechanisms.

The influence of bacteria and sulfides on pitting will be discussed later.

5. Crevice Corrosion

Intense localized corrosion frequently occurs within shielded areas exposed to certain environments. Shielded areas are expected when porous gaskets are employed, when large dense rocks contact bare pipes, under fractured or disbonded coatings, etc. The mechanism of attack is thought to be similar to that for pitting, except that there is no necessity for initially forming a shielded area. In addition to chloride ion migration and ferrous ion hydrolysis, differential aeration contributes to crevice corrosion (and also to pitting), especially in the early stages. Since oxygen has difficulty moving into a crevice, the concentration of oxygen within the crevice soon falls below that at the external surface. Equation 5 indicates different potentials between the exterior and crevice, making them cathodic and anodic, respectively.

Crevice corrosion of mild steel in NH_4NO_3 solutions was found to be maximum under conditions of weak passivation (485). In crevice corrosion of stainless steel in seawater, it was found that the entrapped corrodent had a pH below two and contained ferrous but not ferric ions (584). Hydrolysis of chromic ions was thought to occur with stainless steel in addition to hydrolysis of ferrous ions to lower pH.

Crevice corrosion of stainless steel only occurred below a critical potential in dilute H_2SO_4. Chloride ions facilitated spreading of attack **(487).**

6. Galvanic Corrosion

It is well known that, when a more noble metal is in contact with iron the corrosion rate of the iron is accelerated because it has a lower potential. Comparison of galvanic corrosion results with standard EMF values shows that this is not precisely true. Galvanic corrosion can only be well understood by studying mixed potential behavior, as illustrated by Figure 5. The main reason the corrosion rate is accelerated is that the cathodic reaction is faster, so that the net anodic dissolution reaction is faster. If the other metal's cathodic reaction is sufficiently fast and its anodic reaction is slow, then it can accelerate the corrosion of iron even though it has a lower standard potential. The magnitude of the effect depends on the relative size of the metals. The iron nearest the foreign metal is affected most severely.

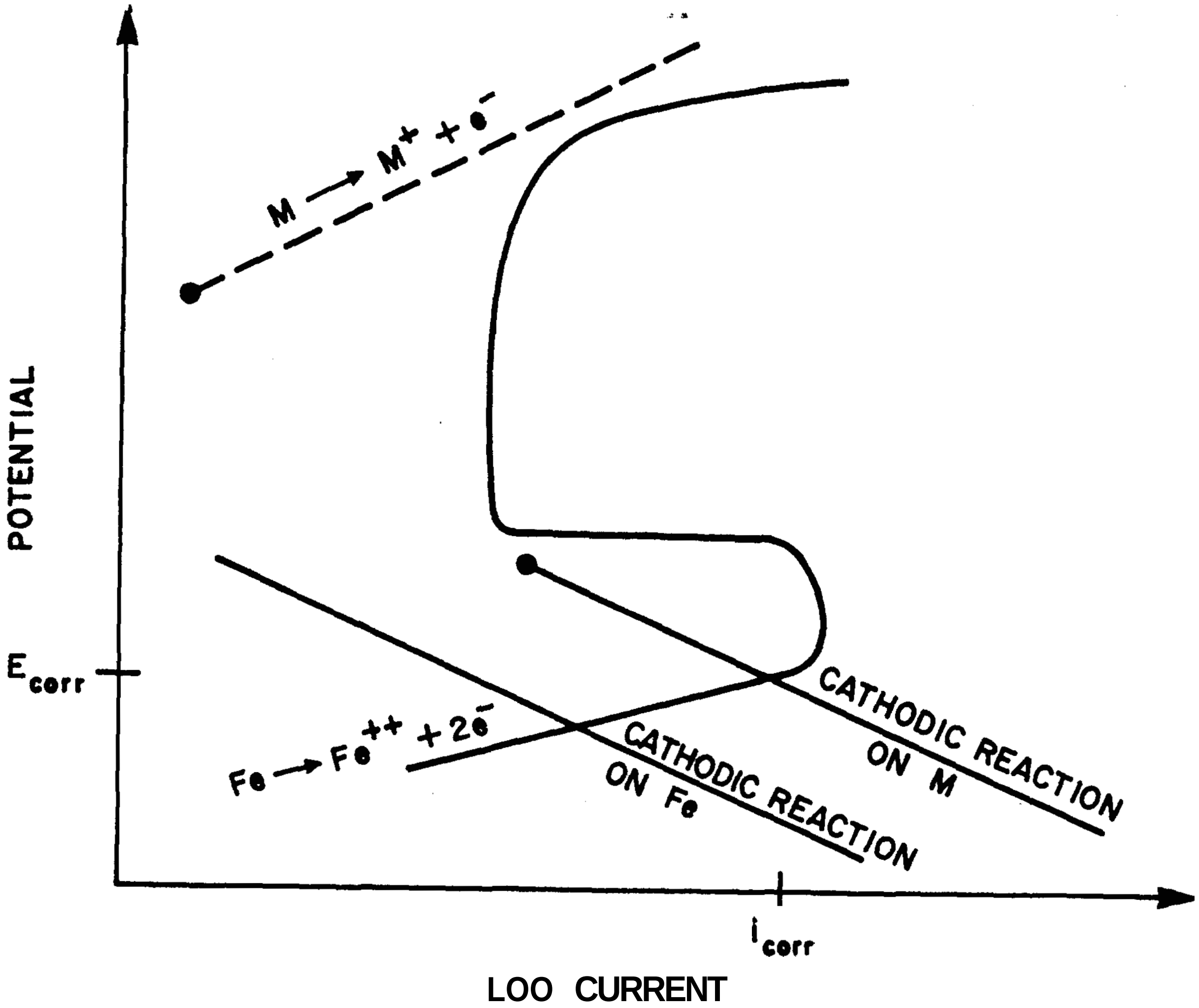

Figure 5. Mixed Potential Curve for Galvanic Corrosion of More Noble Metal M Having Higher Rate of Cathodic Reaction

Even two different steel alloys in contact create a galvanic couple and accelerate corrosion of one of them. Thus, stainless doubled the corrosion rate of carbon steel in aerated 3.5-percent NaCl when the areas were equal and increased the rate by eight to nine times when the stainless had an area eight times as large (784). Certain corrosion products can be cathodic with respect to steel. Thus, for example, new pipe in a rusted line will be anodic and corrode preferentially. A recent survey of pipeline corrosion at 23 U.S. Navy locations revealed that many failures were caused by use of dissimilar metals.

Galvanic cells were named as the most prevalent cause for corrosion by more companies (76 percent) surveyed than any other cause.

7. Corrosion by Stray Currents and High Voltage Direct Current

Equation 1 shows that anodic dissolution takes place where (positive) current leaves the pipe. If electric fields are present in the soil, current will flow in the pipe. Where the current exists, corrosion will take place according to Equation 4. This amounts to 0.55 mils per year for a current density of 1 mA/square ft. If a coating of low electrical conductivity is applied to the pipe, the corrosion will be even more rapid at the holidays because the current is then concentrated in small spots.

Stray currents were second only to galvanic cells in causing corrosion leaks according to the companies surveyed (Table 3).

A major source of stray current is electric railways (333). This can be minimized by using a well insulated roadbed and 100-percent rail return for the DC.

Cathodic protection of one underground structure can induce stray currents and corrosion in nearby structures and is known as "interference." This may be alleviated by joining nearby structures with electrical cable and providing protection jointly. A total of 12,408 drainage bonds between the companies' piping and other structures was reported by the surveyed companies. Many of the bonds contained resistors and diodes to control the magnitude and the direction of the current flow between structures. The largest current was 150 A with. the average for many companies around 7 A per major bond. The majority of the bonds carried 0.5 to 5 A. This implies a minimum of 12,000 amperes being exchanged by the companies participating in the questionnaire survey.

The effect of stray currents on pipes can be isolated by interrupting the electrical continuity of the pipe at intervals with insulating flanges. Indiscriminate use of insulating flanges may cause problems due to differences of potential between the two sections of pipe. Cathodic protection is very helpful but must be coordinated with other nearby cathodic protection ventures, as discussed later. A source of stray current may be determined by using two or more copper sulfate electrodes to find the potential gradient. The vector sum of two such measurements in perpendicular directions points toward the source of stray current (568). It has been pointed out that voltages are induced in pipelines parallel to overhead high voltage AC power lines (701). When cathodic protection with rectifiers is used in addition to the induced AC, a net DC current results. Corrosion can be avoided by arranging the rectifiers so that induced current is drained off into the ground bed. AC itself has been found to accelerate corrosion slightly -- less than 1 percent of that from equivalent DC (354, 683). Others have quoted a figure of 0.1 percent independent of current density (405).

High voltage DC (HVDC) power transmission lines are planned for the near future. Power companies have claimed that earth currents will neither be large nor frequent, and that in any event, the currents will largely follow deep strata in the earth. The pipeline industry and some corrosion consultants disagree

(253, 336). If the pipeline companies fears are realized, litigation for damage is likely. Not only could large currents of even a few minutes duration cause significant corrosion where the current leaves the pipes, but coatings can be damaged where current enters the pipes. Since the power companies only expect to induce stray currents several hours per year, a possible solution with respect to corrosion is for the HVDC system to shut down, rather than divert current into the earth and create a difficult, random stray current situation.

Several tests have been conducted to determine HVDC effects. Currents of 300 A near Los Angeles had little effect on pipes in Los Angeles, presumably because of the high density of pipelines.* Fifty miles from Los Angeles 50 mV changes were observed. However, on some pipelines current was picked up in damaging amounts (260, 523, 252, 727). One surprising result of the Los Angeles measurements is the random telluric currents that were found. These are thought to be due to such sources as small shifts in the earth's magnetic field and fluctuations in cosmic rays. A study on telluric effects concluded that corrosion is insignificant for coated, protected lines and bare lines (794).

Use of HVDC deep well electrodes does not necessarily limit the risks of stray current (252). The location of the electrodes in relation to pipelines was found to be critical. Location of electrodes in the sea was found to be best. More tests are needed and are under way (727).

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* September 1969 meeting of Los Angeles Cathodic Protection Committee.

A computer study showed that currents do not plunge to the core of the earth. Depth of burial, soil resistivity, and pipe were found to have little effect on interference effects. Larger diameter pipe showed larger effects. The distance of the pipeline from the HVDC electrode was found to be the major factor in determining the effects on a pipeline (488).

Although cathodic protection is useful against normal interference, the HVDC currents are expected to change so rapidly that ordinary manually adjusted systems cannot compensate for them. Large current sources with automatic control will be required -- and will be expensive *(335)*. Automatic control may be required only for up to 150 miles from the HVDC electrode (795).

A study was made of a hypothetical pipeline 36 inches in diameter and 250 miles long, with 50,000 ohms-square foot coating resistance (796). The pipeline was assumed to be in the electrical field established by HVDC earth currents and separated 20 miles from the electrode. Under these circumstances, a problem of corrosion and disbonding would exist. The study concluded that: (1) HVDC effects can at best only be mitigated at considerable expense: (2) because of the wide fluctuation in the amperage of HVDC current, automatic regulation of protective currents would be necessary over the length of the buried structures; (3) for the hypothetical pipeline studied, nine controlled rectifier installations would be required at an estimated capital cost of about $200,000.

In another study (797), the literature and "off-the-shelf" equipment were reviewed to determine the best arrangement for correlating HVDC currents with earth currents and cathodic protection currents. For about $5,000 per assembly, equipment can be put together from available commercial components. Required would be a high impedance digital voltmeter, a paper tape punch, and appropriate switching and multiplexing equipment to measure several potentials at one time. The package could operate unattended for an extended period of time on AC power (797).

8. Mechanical Stress Effects

Steel can be made to fail both by corrosion and by application of sufficient mechanical stress. When both stress and a corrosive environment are applied simultaneously, failure occurs at lower levels of stress and/or sooner than when either act alone. Severe cracking sometimes results from the action of certain corrodents on certain metals when a tensile stress is applied.

Table 3 shows that a small but significant fraction of the companies surveyed consider mechanically aided corrosion to be a prevalent cause of leaks.

Some corrosion engineers distinguish between two types of cracking -- stress corrosion cracking and hydrogen embrittlement or hydrogen stress cracking -- while others do not. It is thought by some that stress corrosion cracking is due to stress-accelerated dissolution at the tip of the crack and that cathodic polarization can eliminate the phenomenon. On the other hand, hydrogen stress cracking is attributed by some to hydrogen atoms diffusing into the iron and embrittling it so that it cracks easily. Cathodic polarization would worsen this phenomenon, while anodic polarization would relieve it. Caustic embrittlement is thought to be hydrogen embrittlement engendered by a high pH environment.

Related to other hydrogen effects is hydrogen blistering in which blisters are formed in the metal. Blisters generally occur at elevated temperatures. Wet hydrogen sulfide can cause stress cracking called sulfide stress corrosion cracking (337, 338). One important difference between this and other forms of stress cracking is that the environment in sulfide processes is usually inside the pipe rather than external, as with most other corrodents. Hydrogen sulfide is found in sour gas, crude oil, swamps, marshes, and open sewage disposal areas.

Corrosion fatigue refers to accelerated failure caused by stress cycling due to the presence of a corrosive environment. The exact mechanisms responsible for these phenomena are uncertain and may not always be the same. These phenomena are under very active investigation, partly because so many unanswered questions remain and partly because failure can be catastrophic.

In pipelines stresses arise from internal hydrostatic pressure, bending in irregular trenches, backfill, etc. Residual stresses are also present from plastic deformation in manufacture and pipelaying. Even the thermal stresses of welding produce residual stresses. In 1965 a 24-inch natural gas pipeline failed from stress corrosion cracking and 17 people were killed (694). A recent survey showed that stress corrosion cracking was observed in a variety of pipelines (586). Failures and nearby secondary cracks were axial and not associated with welds, pitting, general corrosion, or any other defect. Cracks followed grain boundaries and contained black Fe_3O_4 crystals. Failures occurred on both bare and coated pipes, although disbonded coatings were often associated with cracking. Differences in the amount of cracking were noted between different lots of pipe steel but could not be explained. In general the tendency to crack increases with yield strength. Hydrogen stress cracking was found not to be a problem unless yield strength exceeded 130,000 psi (587). The few service failures in gas transmission lines due to hydrogen stress cracking were initiated at inadvertent hard spots or hard weld zones with ultimate strengths over 175,000 psi. Hard spots in pipe are usually detectable as flat regions in the pipe. Sulfide cracking also increases as yield strength increases (337). Hard electric resistance welds have been known to crack for hundreds of feet in the presence of internal hydrogen sulfide (338).

Table 8 indicates the total number of leaks caused by hydrogen blisters and cracks that the 373 operating companies have experienced. The questionnaire asked the respondants to explain the existing exposure conditions for each leak or crack, such as tenperature of pipe, vibration, pressure, pipe potential, presence of nicks or scratches, hard spots, analysis of cause of crack,

TABLE 8

NUMBER OF CORROSION LEAKS THAT HAVE BEEN CAUSED BY HYDROGEN BLISTERS AND CRACKS

	Number of Leaks						
	1	2	3	4	6	17	100
	Number of Companies						
(A) Hydrogen Blisters	3	1	0	0	0	1	0
(B) Cracks	8	1	1	0	1	0	1

such as hydrogen stress cracking or stress corrosion cracking, etc.

The following quotations are some of the more interesting explanations:

(1) "The two hydrogen blister leaks occurred in areas of high CO_2 and H_2S content co-existing with free water in the gas stream upstream of a process plant. It was determined by an independent laboratory that hydrogen atoms penetrated vast laminations in the pipe and resulted in pressure build-up within the laminations. In this respect, corrosion was a contributing factor to the leaks. It was estimated that upwards of 25 percent of the pipe area was laminated in the affected area. The entire systems involved were taken out of service, hydrostatically tested, and ultimately the entire systems were returned to service. Dehydration equipment was then installed at well-heads to dry the gas streams. Inhibitors were used during the interim period and continue to be used as a safety factor." (Q533)*

(2) "In 1951 and 1952, we had 17 failures in the gathering system due to hydrogen blisters originating from generation of hydrogen from the corrosion processes of the acid gas (CO_2 and H_2S content) being gathered." (Q636)

(3) "One leak incident has been attributed to stress corrosion cracking based on the characteristics of the observed secondary cracks, fracture in the field and in the laboratory. The information on this investigation has been included in

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* Numbers in parentheses preceded by "Q" refer to information from specific questionnaires.

the NG-18 Pipeline Research on Stress Corrosion Cracking. The environmental factor which promoted the cracking has not been identified. Hardness, tensile properties, and chemical properties of the steel were normal. The operating stress was well below the yield strength of the steel. The pipe was bare (except for mill primer) and cathodic protection had been installed one year previously. The actual pipe-to-soil potential at that time is not known. Chemical analysis of the soil did not reveal any unusual constituents." (Q663)

(4) "Both cracks occurred in a hard spot which had an area somewhat equal to this sheet. The mass hardness was Brinnell 477." (Q341)

(5) "One crack with the following exposure conditions:

Pressure 960 psi
Temperature 110°F to 115°F
Installed in 1959
Pipeline Coating - Polyken Tape #900
Type Pipe - X-52
Cathodic protection installed 1959
Cathodic protection potential - 1.8 to -2.0 volts" (Q384)

(6) "Two cases of stress corrosion cracking with the following exposure conditions:

Temperature - 45° - 60°F
Pressure - 500 lbs/in^2
No vibration, nicks or scratches, or hard spots
Pipe-to-soil potential 2 volts" (Q439)

(7) "On 100 cast iron leaks, the pipe was cracked. We do not know whether the corrosion caused the cracks or the cracks caused the corrosion." (Q144)

(8) "One crack due to selective corrosion in a longitudinal seam of electric resistance welded pipe." (Q580)

Some recent research results on stress-corrosion phenomena are reviewed briefly in the following paragraphs.

Pipeline steel was heat treated to obtain yield strengths ranging from 110,000 to 150,000 psi. Cracking occurred at stress and cathodic protection conditions like those that might be used with high strength steels. Susceptibility to hydrogen stress cracking depended on the rate at which hydrogen atoms entered the steel, which in turn was generally larger at high pH (356). Ductility and tensile strength of stainless steel foils were reduced by atomic hydrogen absorption during cathodic charging (332). In single crystal iron the hydrogen atom penetration rate decreased as the packing density of the plane parallel to the surface increased (199). It was found that hydrogen solubility in iron and steel was increased by tensile stress and decreased by compressive stress (387). Diffusivity was unaffected. Beyond a critical concentration, which depended on temperature, hydrogen produced structural damage and embrittled the metal. Iron sulfide films retarded hydrogen penetration (385).

The susceptibility to failure of 9-4-45 high strength steel was observed to increase with both anodic and cathodic polarization (407). It was suggested that hydrogen embrittlement may be involved in all stress corrosion cracking. The pH at the tip of a crack as a function of potential in salt water was measured, and it appeared that conditions were always favorable for hydrogen reduction (400). Electron microscopy revealed no difference in fracture features at different potentials. A model has been proposed which requires H_2 liberation at the crack tip (548).

It has been suggested that plastic deformation at the tip of the crack increases the rate of dissolution at the tip. However, cold work has been found to have no effect on the corrosion rate of pure iron (756, 759). Carbon additions caused the rate to increase with cold working, especially at normally passive potentials (756, 316). High temperature annealing reduced the rate, suggesting that lattice imperfections by themselves do not cause increased corrosion but that compositional inhomogeneities do.

Studies of structural changes in AISI 4340 high strength carbon steel suggested that the effect of hydrogen is to reduce the austenitic grain boundary energy (800). Hydrogen in high purity iron causes surface blistering and some internal fissures at grain boundaries (681). The yield stress was lowered, even after hydrogen removal. This suggests that embrittlement is due to dislocation creation and not to dislocation locking.

Measurements of local electrical potentials showed that stresses do not lower the potential at the points of stress concentration in corrosion fatigue experiments (629). When a crack forms, then the potential decreases. Cathodic polarization was deduced to protect not by suppression of local currents but by formation of an alkaline environment causing passivation. On the other hand tensile stress shifted the cathodic polarization curve of AISI 4340 steel in 3 percent NaCl in the more noble direction (484).

Initiation of cracks has been related to defects in the surface film, somewhat similar to pit initiation (288, 485). Use of radiotracer Cl showed indications of charged areas on the surface of the steel, possibly due to sulfide inclusions (306). Seven micrograms of Cl^- on one charged area were sufficient to start corrosion and subsequent surface cracks.

A considerable increase in acidity was found at the tip of an advancing crack in seawater, indicating a mechanism akin to that for pitting and crevice corrosion (596, 774). Fe^{2+} but no Fe^{3+} was detected in the crack (774).

9. Intergranular Corrosion

Grain boundaries in metals tend to be particularly sensitive to corrosion because the energy of the metal is greater there and because impurities tend to concentrate between crystallites. When attack is strongly preferential for grain boundaries, it is known as "intergranular corrosion" and leads to rapid failure. Austenitic stainless steels are particularly susceptible. Heating in certain temperature ranges causes sensitization, whereas annealing in other temperature ranges can eliminate the problem. Unfortunately, sensitization often occurs during welding. Corrosion failure is then known as "weld decay." Addition or subtraction of certain elements can reduce or eliminate the problem.

One proposed mechanism for intergranular corrosion of austenitic stainless involves chromium carbide precipitation at grain boundaries with depletion of the neighboring steel in chromium (769). The chromium depleted areas are then anodic with respect to the remainder of the steel and dissolve rapidly. Not everyone agrees with this mechanism. Intergranular corrosion was found to occur only when the carbides formed a continuous path and not when they formed as isolated crystals (534). It also occurred when high temperature treatment removed precipitates but left high solute concentrations along the grain boundaries. Other workers observed intergranular corrosion only when precipitates were present (535).

10. Influence of Temperature, Velocity, and Time

Temperature influences electrochemical reactions in several ways, although the net effect is generally for corrosion to accelerate as temperature increases. Thus, in H_2S, low alloy steels corrode according to an Arrhenius relationship; i.e., the corrosion rate was proportional to exp (-10,720/T) where T is in degrees Rankine. A maximum rate is often observed in neutral electrolyte solutions at about 70°C (776). The tendency of austenitic stainless to stress crack increases with temperature (691).

The equilibrium potential for an electrochemical reaction changes with temperature, dependent on the entropy of the reaction. In Equation 5, E^o is a function of temperature. The dependence of E on concentration increases as temperature increases by virtue of the last term in Equation 5. Another effect of temperature is to accelerate all chemical reactions. A third effect is to increase diffusion rates, both in the solution next to the metal and through any film covering the surface. The solubility of oxygen decreases as temperature increases, which tends to reduce the corrosion rate.

Stress corrosion cracking has been reported to be a problem in pipe leading from compressor stations, presumably because of the elevated gas temperatures generated by compression.

Underground corrosion of steel has been found to be negligible in permafrost soils (550). In soils subjected to high temperatures, corrosion is increased unless rainfall is so sparse that the water content of the soil is low because of evaporation. A pipeline carrying hot spring water exhibited unusually rapid corrosion (149).

Increases in solution velocity near the metal lowers the resistance for mass transfer, both for transport of reactants to the metal surface and for removal of corrosion products (1). Whether this increases or decreases the corrosion rate depends on what is controlling the rate. If the steel is near the passive state, then increased velocity could increase oxygen concentration at the surface, cause passivation, and reduce corrosion. Flow of th solution will also tend to remove the concentrated solutions necessa for pitting and crevice corrosion. In the laboratory, flowing seawater was found to be more corrosive than quiescent seawater for 304 stainless (584). On the other hand, stainless corrodes more slowly near the surface of the ocean than in deep quiescent seawater, which is much lower in oxygen content. Stirring reduced deposition of ferrous hydroxide film in 0.1 N borax (327). If particles are present in the fluid, passive films can be damaged and corrosion greatly accelerated as velocity increases. This is known as "erosion corrosion." With high purity water flowing in mild steel tubes, corrosion increased with velocity up to a certain value and then decreased (309). This indicates different rate controlling steps in the two regimes.

Uniform corrosion tends to decrease with time because of the presence of corrosion products blocking access of corrodents. On the other hand, pitting and stress cracking increase with time. Chloride-induced breakdown of passive films requires an induction time, which decreases as temperature increases (773). From an empirical standpoint the corrosion failure rate of unprotected pipelines tends to increase in an exponential manner with time.

11. Effect of Solutes

The role of various ions in corrosion of iron and steel was recently reviewed in Reference 777. The situation is complex because so many factors are involved in determining the corrosion rate. There are also an infinite variety of combinations of different solutes and conditions. Nevertheless, it is possible to state a few general principles and summarize the observations. One can see from the cathodic reactions, Equations 2-3, that corrosion should be accelerated by low pH and by higher oxygen concentrations at the surface. Although increasing H^+ concentration increases corrosion, the anodic polarization curve of Figure 2 is actually shifted to the left, with current density change proportional to $1/a^2_{H^+}$, where a_{H^+} is the activity of H^+ (389). It has been suggested both that OH- catalyzes the anodic reaction (Equation 1) and that H^+ inhibits the anodic reaction. The influence of oxygen on rate was often ignored in early experiments, and so contradictory results were often obtained for the influence of electrolytes on corrosion. At low concentrations the corrosion rate is often found to be proportional to the square root of concentration (776, 777). This probably reflects the influence of the conductance of the solution, since corrosion involves movement of electric charge through the solution and will increase as conductance increases. Typically, corrosion rate increases with concentration only to a certain point and then diminishes as concentration is increased further. For "aggressive" anions such as Cl^- the maximum occurs at about 0.5 normal. For "passivating" anions it occurs at a lower concentration in the neighborhood of 1-10 ppm. The reason for falloff with higher concentration of aggressive ions apparently are (1) reduced oxygen solubility, and (2) changes in corrosion product films. Corrosion is reduced with higher concentrations of inhibitor ions because of surface **adsorption.**

The type and. stability of any film formed on the surface of steel has a very large effect on corrosion. The film properties depend in turn on the solutes present. Thus, soluble cations have only a small influence on corrosion rate, while cations such as Zn^{++} form an insoluble product at cathodic areas **and** greatly reduce corrosion. If the reaction products are soluble, corrosion stays at a high rate, while the rate decreases if insoluble products are formed.

Corrosion is accelerated by ions which pass easily from one valence stare to another, such as

$$Fe^{3+} + e^- = Fe^{2+} \qquad \text{(Eq. 8)}$$

This reaction acts as an additional cathodic reaction. Fe^{2+} is reoxidized to Fe^{3+} by oxygen. Cations of noble metals such as Cu are displacement plated onto steel and accelerate corrosion by galvanic action. The presence of other metals in the general neighborhood of the pipe can influence corrosion by changing the composition of the soil **(786).**

Results are difficult to predict for mixed solutes. Neutral salts were found to increase H^+ activity and so to reduce the anodic reaction rate **(389).** In sulfuric acid, NaI, NaBr, and NaCl inhibited, while NaF accelerated corrosion. Ten percent HCl, NaCl, and LiCl accelerated corrosion, while $FeCl_2$ inhibited. Chloride ions altered the structure of films formed in NO;. Breakdown of previously formed passivity occurred only above a "breakthrough" potential in borax-chloride solutions, which became more negative with increases in Cl^- and more positive with increases in borax concentration **(329).** Below the "pitting" potential, Cl^- produced no changes in passive films (401). While NO; and $CrO_4^=$ inhibited corrosion, the amount required increased as Cl^- and $SO_4^=$ concentrations increased **(775, 776).** To produce a given corrosion rate, passivator concentration C_P was found to be related to aggressor concentration C_a by

$$\log C_P = a + b \log C_a \qquad \text{(Eq. 9)}$$

This indicates a competitive adsorption mechanism. Corrosion rate remained low as pH was decreased to **2.8** if $HCrO_4^=$ was employed to lower pH, while **it** increased below pH **5** if H_2SO_4 was used to reduce pH **(776).** On the other hand, halides enhanced organic amines' inhibitor efficiency, most notably with I^- (343). Both H_2S and Cl^- accelerated corrosion at 150°C, but their effects were not additive (706).

Solutes can also play a significant role in hydrogen absorption phenomena such as embrittlement, stress cracking, and blistering. For example, oxidized arsenic compounds increased hydrogen absorption (399). This was thought to arise from hindrance of the combination of liberated hydrogen to form molecular hydrogen, which is competitive with absorption.

12. Underground Corrosion

Many studies have been made on corrosion of bare unprotected ferrous metals buried in various types of soil for periods of up to 45 years (282, 429, 525, 539, 550, 551, 552, 639, 678, 687, 778, 788-790). Field tests were shown to be necessary from the observation that pitting was many times greater in the field than for the same soil in the laboratory. Various soil parameters, such as pH, electrolyte concentration, moisture content, resistivity, etc., were determined and attempts made to correlate corrosion rate with such parameters. Moisture, which is generally more abundant in poorly aerated soils, provides the electrolyte for the corrosion process. The electrolyte is composed of hydrogen and hydroxyl ions from the water itself, and a variety of cations and anions that depend upon the soluble salts dissolved in the soil. These ions determine the electrical conductivity, or resistivity, of the soil and the chemical properties such as acidity and alkalinity.

The kind and concentration of soluble salts in soils seem to affect the initial rate of corrosion and the progress of corrosion with time. In general, the most corrosive soils contain large concentrations of soluble salts, especially in the form of sulfates, chlorides and bicarbonates, and may have very acid or highly alkaline pH values. Such soils also have relatively high conductivities, or low resistivities. The least corrosive soils, as a group, have high resistivity values, which indicate low concentrations of soluble salts. Since resistivity measurements provide as much information as any other single soil property regarding the corrosive characteristics of a soil, and since it can be readily measured, it is often used to provide approximations of the corrosivity of soils. Resistivity measurements have still greater value when supplemented by observations of soil drainage and/or measurements of pH. In general, soils with resistivities greater than 5,000 ohm-cm are found to be mildly corrosive to noncorrosive. It should be realized, however, that because many other factors may affect the corrosion rate of metal, certain high resistivity soils nay be more corrosive than soils of lower resistivity (552). Instances have occurred where change in soil resistivity, rather than the absolute value, has been found to be the major cause **of** corrosion.

It has been found tnat the resistivities of most soils exhibit a logarithmic normal distribution, i.e., that the cumulative distribution of the logarithms of many resistivity measurements along a pipeline right-of-way falls on a straight line on probability paper. Such **a** soil is defined as "statistically uniform."

In one study, pits were found only at points where resistivity was below about 1200 ohm-cm, with increasing frequency below that (763).

Rates appeared to increase as pH increased, although pH also tended to increase with decreasing resistivity. Another study revealed no correlation with pH, water holding capacity, or salt concentrations for various irons and steels (639). Tests of nickel cast iron samples revealed no correlation with moisture, resistivity, pH, or Cl^- content (525).

Oxygen availability has a large influence on corrosion rate. It has been found that undisturbed soils are so deficient in oxygen a few feet below the ground line or below the water table zone, that steel pilings were not appreciably affected by corrosion, regardless of the soil types or properties (539). Unfortunately, pipelines are almost invariably found in trenches, where the soil has been disturbed.

Temperature can have a significant effect. Thus, steel piles in Alaska showed no corrosion when buried in permafrost (below 5 feet) for 6 to 11 years (550). A few pits were found in the active thaw region (about 5 feet) and ranged up to 0.7 mm in depth. (It should not be concluded from this that oil pipelines in permafrost will not corrode, since they will be warmed to prevent solidification of the oil). Conversely, serious problems were encountered with heat distribution lines below the water table but not with those above the water table (479).

In an extensive NBS program, it was found that the initial pitting rate decreased in well drained, high resistivity soils, but is maintained in poorly drained, low resistivity soils (552). The pitting rate R_p changed with time θ according to

$$\log R_p = \log k + n \log \theta \qquad \text{(Eq. 10)}$$

where n = 0.19 for well aerated and n = 0.68 for poorly aerated soils.

The following equation was derived for maximum pit depth in mils (754):

$$p = K_n K_a (10 - pH)^n (\theta/\rho)^n A^a \qquad \text{(Eq. 11)}$$

where pH is the soil pH, ρ is the soil resistivity in ohm-cm, θ is time in years, and A is the exposed area in square feet. K_a and "a" are dependent on the alloy used, as shown in Table 19. Theoretical values for n were derived by considering the probable rate limiting step. They compare well with the NBS empirical values in Equation 10. Thus, in well aerated soils n = 1/6 for $CaCO_3$ film formation on cathodic areas being rate limiting. For fairly aerated soils n = 1/3 for formation of ferric corrosion products over the pit. For poorly aerated soils n = 1/2, which is an area effect with constant corrosion current. In very poorly aerated soils the corrosion products are soluble and lower the resistivity of the soil electrolyte, leading to n = 2/3. Comparison with NBS field experience gave values of K_n = 170, 222, and 355 for good, fair, and poor soil aeration,.

A Soviet study indicated that the number and depth of pitting of gas pipelines increased with increasing frequency of changes in soil properties with distance (730). Changes in elevation, soil type, and resistivity were considered. Greatest pit depths were caused by alternating from clays to sandy soils.

13. Gas and Petroleum Corrosion Effects

Seventy-three of the oil and gas operating companies responding to the questionnaire transport materials which, in the presence of free moisture, may cause internal corrosion. Table 9 lists the materials transported by these companies.

Corrosion in oil and gas well equipment was reviewed in Reference 553. Corrosion was primarily internal. Sour oil and gas contain H_2S, while sweet oil contains only CO_2 and fatty acids. Sweet corrosion is associated with high saltwater production,

TABLE 9

MATERIALS TRANSPORTED WHICH CAUSE INTERNAL CORROSION
IN THE PRESENCE OF FREE MOISTURE

Material	Number of Companies
Sour Crude (H_2S)	22
Sweet Crude (CO_2)	14
Crude oil	7
Water	6
Saltwater	5
Sulphur	4
LPG	3
Refined Petroleum Products	3
Casing head, gas, & fracking solution	1
Caustics	1
Cl_2	1
Gasolines	1
SO_4	1

i.e., 40 to 50 percent. A CO_2 pressure of over 30 psi usually caused corrosion, while pressures below 7 psi were noncorrosive.

The general corrosion rate of low alloy steels in aqueous H_2S solutions increases as the H_2S concentration increases. Hydrogen sulfide in sour wells caused corrosion by producing cathodic iron sulfide and by hydrogen cracks and blisters (553). It has been noted previously that H_2S can induce stress corrosion cracking. On the other hand, iron sulfide films produced on iron by H_2S-CO_2-H_2O corrosion were protective (374). Studies of pH effect showed that film was least protective in pH range 6.5 to 8.8 and essentially contained kansite (Fe_3S_4). The most protective film also contained pyrite (FeS_2) and troilite (FeS).

The corrosivity of petroleum increases as its water content increases. In fact, there is very little or no corrosion unless moisture is present (706). A 1953 survey showed required maintenance of 348 sweet wells in California increased irregularly as the percentage of produced water increased (6183). Water in low spots in pipes is especially deleterious particularly with sour oil and gas. Such water is eliminated or reduced by proper design and by periodically pigging the line. The determination of safe limits for H_2S, CO_2, and H_2O contents in relation to pipe grade, operating pressure, stress level, etc., are needed (Q126).

14. Corrosion in Natural Waters

Offshore oil production has increased dramatically in recent years. Accompanying this has been an increased public sensitivity to marine oil leakages. Pipelines also cross rivers, harbors, bays, etc. Some of these environments are very corrosive.

Although seawater is approximately equivalent in strength to 3.5 percent NaCl (0.6 normal), many other components are present, as shown in Table 10. The pH varies from 8.1 to 8.3. The corrosion behavior of seawater is also appreciably different from 3.5 percent NaCl. A critical factor in corrosivity is the oxygen content, which decreases with increasing temperature, increasing depth, and increased stagnance (779). Attack of mild steel is less at great depths, while stainless steel is corroded less at high oxygen concentrations. The splash and tidal zones are most corrosive for ordinary steels (784). Coastal and harbor waters are more variable in composition and more corrosive. Forty-seven percent of steel pilings submerged for 37 years in San Francisco Bay had severe corrosion with broad pits of an average depth of 0.1 inch (138).

TABLE 10

COMPOSITION OF SEAWATER

	ppm
Cl^-	18,980
SO_4^-	2,649
HCO_3^-	140
Br^-	65
F^-	1
H_3BO_3	26
Na^+	10,556
Mg^{++}	1,272
Ca^{++}	400
K^+	380
Sr^{++}	13

Fresh waters vary in corrosivity. Soft waters are more corrosive than hard waters, probably because of precipitation of calcium salts from hard waters. Excess CO_2 and low pH enhance corrosion by preventing precipitation of protective carbonate films. Polluted waters sometimes contain NH_3, H_2S, or SO_2, all of which may increase attack.

Marine pipelines may pass through different zones of soil conditions, aeration, etc. Concentration cells formed between two zones cause "macro-corrosion," which is more serious than the "micro-corrosion" caused by conditions within a single zone (241, 160). The macro-corrosion rate has been found to increase rapidly as the ratio of cathodic area to anodic area increased.

15. Biological Effects

Living organisms can have large influences on corrosion of ferrous metals. The deleterious influence of some marine organisms is readily apparent. For example: Purple sea urchins remove rust coatings, and thus accelerate corrosion; pitting is favored under barnacles. Such fouling is much less severe at 5500 ft than at the surface (254).

The effect of micro-organisms is difficult to isolate and to determine. It is known that they are present under ground, in natural waters, in sewage, and probably also in some petroleum products. Sigh populations have been found adjacent to pipelines (5025). Green algae can create oxygen supersaturation which accelerates cathodic reactions and forms concentration cells. Bacteria consume oxygen and generate cells when organic food is present, such as found in some coatings (174). Alternate bands of aerobic-anaerobic zones are found in sediments containing, different amounts of organic materials. This is very corrosive. Sulfuric acid is generated from sulfur and sulfides (780). pH levels of 5 and 6 have been produced by generation of humic acids in the soil. CO_2 is a universal metabolic product of all saprophytic microbes. Ammonia can be produced by bacterial hydrolysis of urea.

The most studied micro-organisms from a corrosion standpoint are the sulfate reducing bacteria (780, 538, 549, 524, 375). These anaerobic bacteria reduce $SO_4^=$ to H_2S, which is in itself corrosive. Iron sulfide-iron cells are also formed. However, the main influence seems to be direct depolarization or acceleration of the cathodic reaction.

The schematic of Figure 4 obviously does not apply to corrosion which results from bacterial reduction of sulfate ions. Little has been published on the composition of the consequent corrosion product. However, since the reduction occurs under anaerobic conditions, ferrous sulfide would be expected as the prevalent form. But both **it** and the light colored ferric sulfide, both comparable in formula to the corresponding oxides, are highly insoluble. The mantle often takes the form of a slab defining, no doubt, the extent of the bacterial proliferation. The slab is used by some as an item of identification of hydrogen sulfide corrosion.

Sulfate reducers (desulfovibrio) produced Fe_2P and a volatile phosphorous compound when growing in contact with steel and phosphates (538, 549). Soil bacteria in contact with bare steel generated potential differences in the lab (5025, 5023). Light increased the corrosion rate. Methane-generating bacteria also increase the corrosion rate (4).

The importance and prevalence of this type of corrosion have long been in question. One extensive random inspection of coatings on a pipeline from the southwest to the eastern seaboard failed to discover sulfides in the soil. Table 3 shows that 24 percent of the companies surveyed consider microbiological corrosion to be a significant cause of leaks. Table 11 exemplifies the uncertainty in extent of bacteriai corrosion.

The uncertainty can also be shown by quoting from respondents to the questionnaire:

(1) "One of our consultants (claims) this as a major cause of corrosion. Other consultants have since expressed doubts as to the validity of his assumption." (Q625)

(2) "We find . . . that anaerobic sulfate reducing bacteria are the major cause of corrosion." (Q357)

(3) "We believe that majority of all corrosion leaks on steel pipes (is) caused by sulfate reducing bacteria." (Q500)

TABLE 11

COMPANIES EXPERIENCING BACTERIAL CORROSION

	Yes	No	Do Not Know	Rarely
(A) Anaerobic	37	120	158	33
(B) Aerobic	9	134	173	16

(4) "We do not consider that it ever has been demonstrated that bacteria cause corrosion on pipelines." (Q585)

Many of those who attribute corrosion to bacterial action base their conclusion on the presence of sulfide ion in the soil, not on a detailed examination of the corrosion product mantle. This simple and profitable way to determine the local cause of corrosion has been neglected.

16. Atmospheric Corrosion

Portions of every piping system are above ground at pumping stations, end points, etc. Although corrosion is not as great a problem aboveground as underground, it is present nonetheless.

At low pressures of dry oxygen, an iron oxide film first forms at a linear rate and then approaches a limiting thickness of 26 Angstroms. Traces of water vapor lower the limiting thickness to 18 Angstroms (102). Under real atmospheric conditions corrosion is similar to that found underground. Water is, of course, necessary for these corrosion processes. Rainfall supplies occasional moisture. At a tropical marine site corrosion was more rapid in periods of high rainfall and high humidity (234). Once corrosion products have formed, they can store water by shielding it from evaporation, by forming solutions with lower vapor pressures, etc. It was found that corrosion was negligible when the relative humidity was held below 40 percent with the steel being covered by synthetic rusts containing sulphates and chlorides (781). Hygroscopic salts and acids from the atmosphere can settle on the steel surface and keep it moist. It was suggested that ferrous sulfate hydrate can supply water by dehydration (782).

Many field tests of atmospheric corrosion have been made (e.g., Refs. 189, 43, 169, 234). Corrosivity varies with the metal being tested (189). Sea salt and SO_2 accelerated corrosion (43). Corrosion of a variety of steels was found to be influenced to the greatest extent by SO_2 content (169). Specimens exposed in the winter have a much higher S content at the metal surface than those exposed in the summer (173). SO_2 forms hygroscopic and corrosive H_2SO_4 in the atmosphere and also on the iron surface, which may, in fact, accelerate the reaction.

The influence of airborne salt was illustrated by the observation that the corrosion rate of iron was an order of magnitude greater at 80 feet from the ocean than at 800 feet away (784). Ozone, a component of smog, caused pitting of steel in deionized water but reduced pitting in sea water (785). Ozone also accelerated corrosion of steel in dilute H_2SO_4.