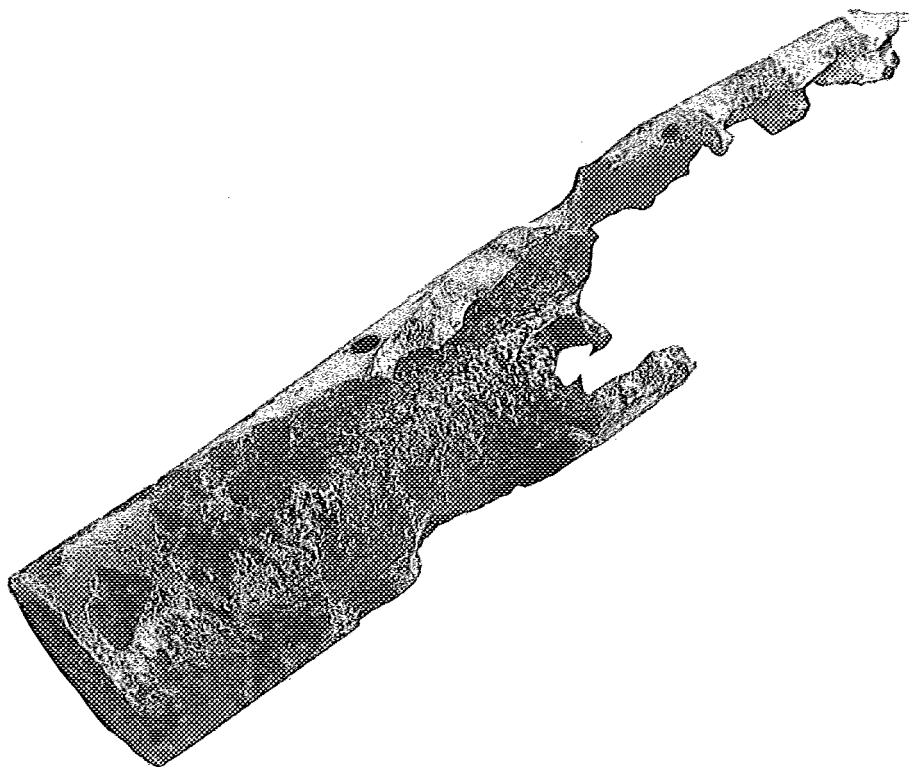# CORROSION OF OIL- AND GAS-WELL EQUIPMENT

BOOK 2 OF THE VOCATIONAL TRAINING SERIES

SECOND EDITION, OCTOBER 1990

PRODUCTION DEPARTMENT
AMERICAN PETROLEUM INSTITUTE

Issued by

AMERICAN PETROLEUM INSTITUTE

Production Department

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Asbestos is specified or referenced for certain components of the equipment described in some API standards. It has been of great usefulness in minimizing fire hazards associated with petroleum processing. It has also been a universal sealing material, compatible with most petroleum fluid services.

Certain serious adverse health effects are associated with asbestos, among them the serious and often fatal diseases of lung cancer, asbestosis, and mesothelioma (a cancer of the chest and abdominal linings). The degree of exposure to asbestos varies with the product and the work practices involved.

Consult the most recent edition of the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Health Standard for Asbestos, 29 *Code of Federal Regulations* Section 1910:1001; the U.S. Environmental Protection Agency's National Emission Standard for Hazardous Air Pollutants concerning Asbestos, 40 *Code of Federal Regulations* Sections 61.140 through 61.156; and the final rule by the U.S. Environmental Protection Agency (EPA), concerning phased banning of asbestos products, 40 CFR Part 763, published at 54 *Federal Register* 29460-29513 (July 12, 1989).

There are currently in use and under development a number of substitute materials to replace asbestos in certain applications. Manufacturers and users are encouraged to develop and use effective substitute materials which can meet the specifications for, and operating requirements of, the equipment to which they would apply.

SAFETY AND HEALTH INFORMATION WITH RESPECT TO PARTICULAR PRODUCTS OR MATERIALS CAN BE OBTAINED FROM THE EMPLOYER, THE MANUFACTURER OR SUPPLIER OF THAT PRODUCT OR MATERIAL, OR THE MATERIAL SAFETY DATA SHEET.

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FOREWORD

The practical value of corrosion countermeasures, no matter how perfect they may be in the theoretical or laboratory sense, depends upon certain knowledge and attitudes on the part of foremen, pumpers, well tenders, and individuals with related responsibilities. This book is directed at field operating personnel, in the hope that steady use will enhance the knowledge and attitudes mentioned, specifically:

Appreciation of the enormous cost of oilfield corrosion.

Ability to recognize early indications of corrosion.

Awareness of the importance of early reporting.

Desire to take effective part in the solution.

The book is not intended to produce technical experts. Therefore, it makes full use of the simplest possible terms and descriptions. The control measures it describes are only typical, and should not be automatically accepted as the best solution for any specific problem. The circumstances of corrosion vary widely, and technical advice should always be sought when causes are obscure, or cost or severity is high.

This second edition was prepared by an Ad Hoc Task Group with guidance and review by the API Production Department Executive Committee on Training and Development. It updates and supersedes the 1958 first edition. The first edition was developed in cooperation with the National Association of Corrosion Engineers (NACE), which later issued a separate publication: NACE TPC Publication No. 5, *Corrosion Control in Petroleum Production.* Personnel needing a more thorough understanding of corrosion technology may obtain that and other technical publications from: NACE, Box 218340, Houston, TX 77218.

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CHAPTER 1

GENERAL ASPECTS OF CORROSION

The useful life of oilfield equipment is often shortened as a result of corrosion. In the last several years great strides have been made in corrosion detection and remedies as applied to the oilfield. This book has been written to put this information in a form easy to use.

In simplified technical terms, corrosion has been defined as the destruction of a metal by either chemical or electrochemical reaction with its environment. Some general statements concerning corrosion rates can be briefly made.

1. Carbon steel will usually corrode faster than corrosion resistant alloys used in the oilfield. There are notable exceptions, such as the failure of strong alloy steels in H_2S systems.

2. The major corrodents encountered in the oilfield are carbon dioxide, hydrogen sulfide, organic acids, hydrochloric acid, and oxygen dissolved in water.

3. Films or scales at the interface between metal and corrodent influence corrosion rates. These films include corrosion products, mill scale, and corrosion inhibitors.

4. Environmental factors — such as chemical composition of water, temperature, and velocity — affect the rate of corrosion. In some cases, so-called natural inhibitors present in produced fluids greatly reduce corrosion rates.

5. Impressed voltages and stray electrical currents are often a source of serious corrosion damage.

6. Velocity of the flowing media plays an important role in erosion/corrosion. It exhibits mechanical wear effects at high velocities, particularly when the media contains solids in suspension.

Types of Corrosion

For practical considerations, corrosion in oil and gas well production can be classified into four main types, each of which will be discussed in a following chapter.

1. CO_2 corrosion is also referred to, and will be referenced in this book, as *Sweet Corrosion*. It occurs as a result of the presence of carbon dioxide. This type of corrosion occurs in both gas-condensate and oil production as well as in produced water handling systems.

2. H_2S corrosion is also referred to, and will be referenced in this book as, *Sour Corrosion*. It is designated as corrosion in oil and gas wells pro-

ducing even trace quantities of hydrogen sulfide. These wells may also contain oxygen, carbon dioxide, or sulfate reducing bacteria.

3. *Oxygen corrosion* occurs wherever equipment is exposed to atmospheric oxygen. It occurs most frequently in offshore installations, brine handling and injection systems, and in shallow producing wells where air is allowed to enter the annular space. The presence of even trace amounts of oxygen in produced fluids containing CO_2 increases the corrosion rate by several orders of magnitude.

4. *Electrochemical corrosion* is designated as that occurring when corrosion currents can be readily measured or when corrosion can be mitigated by the application of current, such as in soil corrosion.

Economics of Corrosion Problem

The annual cost of corrosion and corrosion protection in the United States alone is estimated at approximately eight billion dollars per year. This figure was only for direct costs and no attempt was made to estimate indirect costs due to lost production, safety, and environmental factors. Furthermore, this figure did not take into consideration specific corrosion costs in oil and gas well production. Refinery and pipeline problems were the only aspects of the oil industry considered.

It has been demonstrated many times that where a costly corrosion problem is properly defined, mitigation procedures can usually be initiated with resultant savings to the industry. It should be cautioned that the establishment of a good, scientifically sound, corrosion-control program requires the expenditure of considerable effort by the corrosion expert and the field operating personnel.

We would all like to have a simple magical device which would miraculously cure all the troubles caused by corrosion, as well as every other phase of our lives. There is usually not a short-cut "cure all" treatment to prevent all corrosion problems.

Importance of Field Personnel in Corrosion-control Programs

Certain of the principles of corrosion and corrosion-control procedures have been worked out in corrosion research and engineering laboratories. However, it must be realized that the final success in the battle against corrosion rests on the shoulders of field operating personnel. Their responsibilities in this program can be briefly outlined.

1. *Recognition of the corrosion problem:* Field personnel are in the best position to recognize the onset of corrosion. They know when pulling cost and equipment maintenance costs begin to climb. They further have the opportunity to observe the condition of tubing, christmas trees, casing, pumps, etc., during routine maintenance and inspection.

2. *Record keeping:* Many times the real costs of corrosion are not apparent without up-to-date and accurate records kept specifically for corrosion-control purposes. Certainly the costs and effectiveness of corrosion-control measures can never be ascertained without good records. These records can be kept and evaluated only by field personnel.

3. *Carrying out control procedures:* No matter how well a control system is designed, it is of no value unless it is carefully, regularly, and diligently applied to oilfield equipment.

The experienced corrosion person is always available to assist in the solution of field problems, but is usually in no position to carry out these solutions. This person can help in the selection of the most appropriate corrosion mitigation technique which may include: inhibition; metallurgy; coatings; and cathodic protection. The remainder of this book has been written as a guide to assist the field operator in: *1*, understanding the corrosion problem; *2*, evaluating the severity of the problem; and *3*, choosing and applying proper control procedures.

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CHAPTER 2

SWEET CORROSION

Until recent years, the term "sour crude" was used by production personnel to designate corrosive fluid, and the term "sweet crude" designated noncorrosive fluid. Inasmuch as many of the wells that were previously considered noncorrosive because of the absence of hydrogen sulfide have become corrosive, this distinction has lost most of its accepted meaning. Sweet corrosion, as used here, can be defined as corrosion occurring in oil or gas wells where no iron sulfide corrosion product and no odor of H_2S occurs. Some sweet wells do contain very low concentrations of sulfides.

Controlling corrosion in gas-condensate wells was one of the most pressing problems before the industry several years ago. Expensive workover jobs, damage to the reservoir, and danger to operating personnel all contributed to make this a serious problem. Chemical inhibitors, coatings, and special metal alloys have all been used to combat this problem.

Corrosion in sweet oil wells usually becomes serious after the wells have produced for some years, and is associated with high salt water production. Oil wells usually become corrosive when water production reaches 40 to 50 percent of the total fluid. It is estimated that thousands of gas lift wells will become corrosive and could cost the industry millions of dollars per year in corrosion damage.

DESCRIPTION OF DAMAGE

Chemistry of Reaction

Corrosion in gas-condensate wells is attributed to carbon dioxide and organic acids. Carbon dioxide (CO_2) is noncorrosive in the absence of liquid water. When water is present, CO_2 dissolves and forms carbonic acid.

$$CO_2 \quad + \quad H_2O \longrightarrow H_2CO_3$$
Carbon dioxide $\qquad$ Water $\qquad$ Carbonic acid
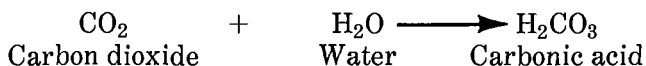
This carbonic acid causes a reduction in pH of the water which makes it quite corrosive to steel.

$$Fe \quad + \quad H_2CO_3 \longrightarrow FeCO_3$$
Iron $\qquad$ Carbonic acid $\qquad$ Iron carbonate
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ Corrosion product
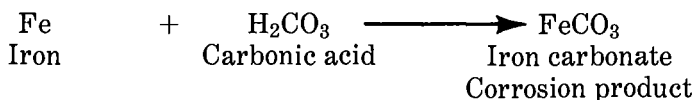
In addition to the acidity produced by carbon dioxide, low molecular-weight organic acids, such as acetic acid, contribute to the corrosion. These acids are seldom considered the primary cause of sweet corrosion.

In general, the preceding statements apply to both oil and gas wells.

However, there is one minor exception. Corrosion has been experienced in some high-pressure, Louisiana Gulf Coast flowing sweet oil wells that produce very little water. This corrosion has been associated with a porous scale deposition containing both chlorides and sulfates. A photograph of typical scales responsible for this type of corrosion is shown in Figure 1. The condition of the pipe after removing the scale and the extent of pitting is shown.

Because carbon dioxide plays such a prominent role in sweet corrosion, some of the factors governing its behavior should be considered. The important factors governing the solubility of carbon dioxide are pressure, temperature, and composition of the water. Pressure increases the solubility (Fig. 2), reducing the temperature decreases the solubility (Fig. 3), and many dissolved minerals may buffer the water (prevent pH reduction). In a gas-condensate well, with almost no dissolved minerals and at relatively high temperatures, pressure is the controlling factor influencing carbon dioxide solubility. In fact, the partial pressure of carbon dioxide can be used as a yardstick to predict corrosiveness of gas-condensate wells.

The partial pressure of carbon dioxide can be determined by the formula:

Partial pressure = total pressure × percent carbon dioxide.

For example, in a well with a *bottom-hole pressure* of 3,500 psi and gas containing 2 percent CO_2:

Partial pressure = 3,500 × 0.02 = 70 psi at the bottom of the well.

Using the partial pressure of carbon dioxide as a yardstick to predict corrosion, the following relationship has been found:

1. A partial pressure above 30 psi usually indicates a corrosive condition.

2. A partial pressure between 3 and 30 psi may indicate a corrosive condition.

3. A partial pressure below 3 psi is considered non-corrosive.

The salt water usually produced by a sweet oil well contains dissolved minerals and the foregoing relationship does not always apply. However, corrosion is most often encountered where the carbon dioxide content is high. As a first approximation, the partial pressure of carbon dioxide is useful in predicting corrosivity of sweet oil wells. In Fig. 4, the solubility of CO_2 in a typical sweet well has been calculated.

Gas-condensate Wells

Corrosion in the tubing of gas-condensate wells usually takes the form of deep pitting, as shown in Fig. 5. The tubing is attacked in sharp, well-defined pits that may penetrate the wall completely in a relatively short

(a) Typical Scale Formation

(b) Appearance of Pipe after Removal of Scale

Fig. 1 — Tubing Corrosion from Wells with Very Low Water Content
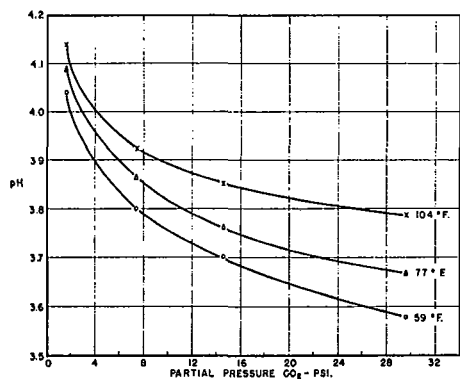

Fig. 4 — Solubility of CO_2 at Various Depths of a Typical Oil Well

Fig. 2 — Effect of CO_2 Partial Pressure on pH of Condensate Water
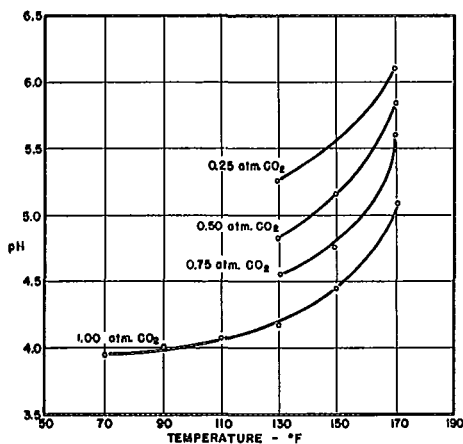
Fig. 3 — Effect of Temperature on pH

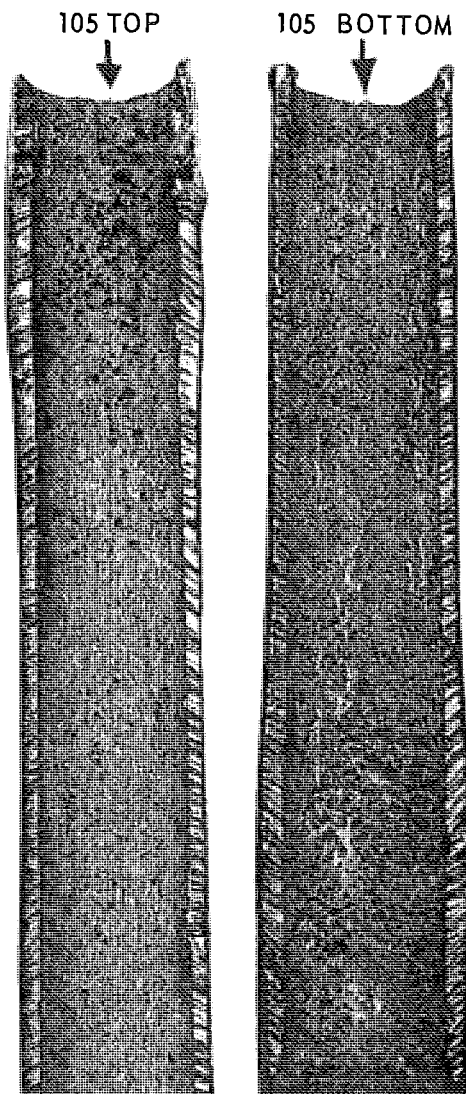Fig. 5 — Gas-condensate Well Tubing — Severe Pitting

period of time. This pitting is caused by acidic gases dissolved in droplets of water condensed on the tubing wall. Tubing below the point of condensation may be relatively free of corrosion damage.

Another type of corrosion sometimes found in the tubing of gas-condensate wells is known as "ringworm" corrosion. As the term implies, the corrosion occurs in a ring a few inches from the upset, as shown in Fig. 6. This corrosion may take the form of very smooth corrosion or severe pitting near the upset. The cause of "ringworm" corrosion has been traced to the upsetting process. The heat required in upsetting causes the heated end to have a different grain structure from the rest of the pipe. A transition zone in grain structure near the upset runout is usually susceptible to corrosion. This condition can be overcome by fully normalizing the tubing after upsetting. Normalizing is a heat treatment that gives uniformity to grain structure. Ringworm corrosion is a common problem with J-55 tubing. Other tubings such as N-80, L-80, and P-110 are normalized to prevent this phenomenon.

Another type of corrosion damage is commonly called "sand-cutting" or erosion. Although sand-cutting does sometimes occur as a purely mechanical action, the damage usually seen is a combination of corrosion *and* erosion. This type of damage is illustrated in Fig. 7 to 10, incl. Damage of this type usually is found near a restriction (such as a choke) where velocities and turbulence are higher than normal. Corrosion products that normally stifle the corrosion reaction are removed and corrosion continues unabated. Erosion/corrosion also occurs where the flow is disrupted such as tee's and short radius ell's. A solution for this type of problem is the utilization of a tee with a bull plug in the running end. As would be expected, damage of this type is most prevalent in the wellhead fittings, but experience has proven that velocity also has considerable effect on corrosion in the tubing. In one field, it was shown that increasing the gas velocity 3.7 times increases the corrosion rate 5 times.

Sweet Oil Wells

Corrosion damage to sucker rods in sweet oil wells may take the form of severe pitting, as shown in Fig. 11 to 13, incl.; or the damage may be in the form of fine cracks that are not so obvious, as shown in Fig. 14. In many areas, pin-and-coupling failures are a major source of trouble (Fig. 15 to 20, incl.). Fig. 21 and 22 show body corrosion-erosion of a coupling and alloy rod.

Damage to the tubing in pumping wells may take the form of pitting, rod wear, or a combination of the two. Pitting of the tubing in sweet oil wells (Fig. 23 and 24) is similar to that in gas-condensate wells. Failures attributed to rod wear are usually the result of both rod wear and corrosion (Fig. 25 and 26). The sucker rod rubs the tubing and removes corrosion products that could stifle the corrosion reaction, thus allowing cor-
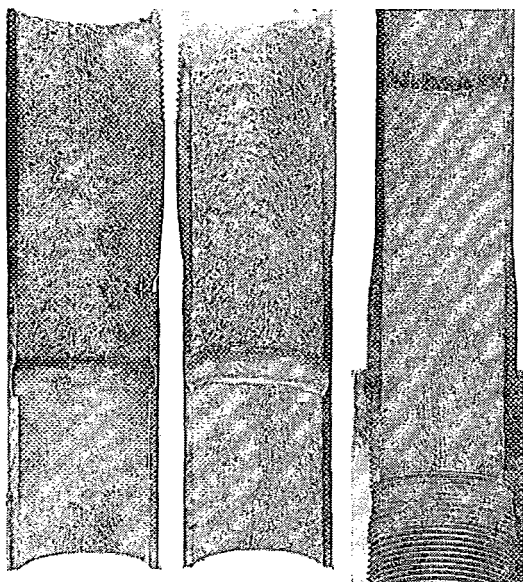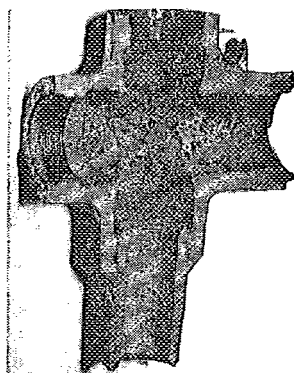
Fig. 6 — Ring-worm Corrosion
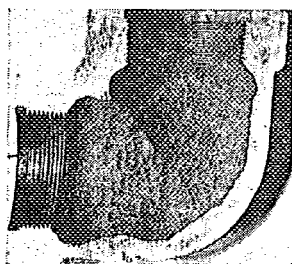
Fig. 7 — Corrosion-Erosion
of Cross-over Tee

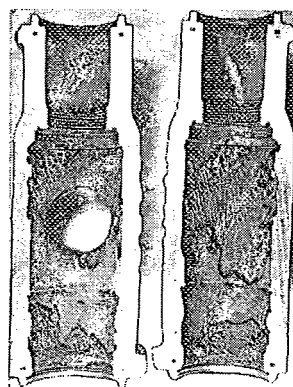Fig. 8 (left) — Corrosion-Erosion
of Ell

Fig. 9 (right) — Corrosion-
Erosion of Choke Body
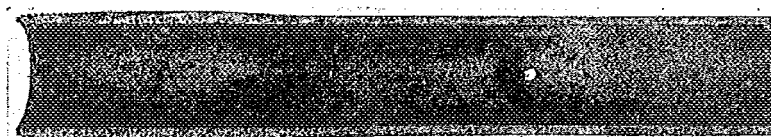
Fig. 10 — Corrosion-Erosion of Tubing Wall Opposite Tubing Perforation

rosion to proceed. The first external evidence of this condition is a split or crack in the tubing wall. The special problem of pump corrosion and wear is discussed in Part 3 of Appendix.

Probably the most serious sweet-oil corrosion problem is in gas lift wells. These wells are usually deep, with high bottom hole pressures and correspondingly high partial pressure of carbon dioxide. They also are usually high water producers. This problem is often accelerated by the injected gas lift gas which may contain small amounts of oxygen. A severely corroded gas lift valve equalizer tube is pictured in Fig. 27. The gas lift problem is doubly severe because it is difficult to get chemical treatments down the annulus and below the gas lift valves. This problem will be discussed in more detail under treating techniques.

METHODS OF EVALUATING THE PROBLEM

A number of tests have been devised to detect corrosion and to determine its severity. The ultimate goal of this work is to be able to predict corrosion before severe damage occurs. By use of all the techniques described below, a reasonable prediction of severity of corrosion can be made.

Iron Content

Analysis of produced water to determine the *iron content* is a useful means of predicting corrosion. However, there are a number of factors that should be considered when using this method of determination. The iron content of water from a gas-condensate well has more significance than the iron content of water from a sweet oil well. This is to be expected, because there is usually very little bottom water to contribute impurities.
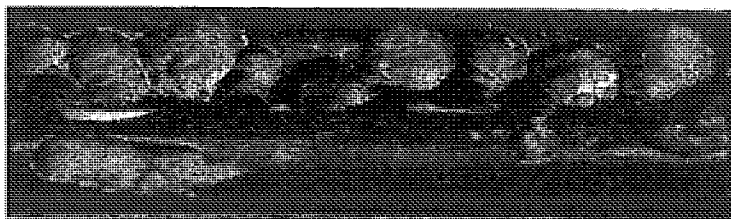
Fig. 11 — Severe Pitting of Sucker Rods
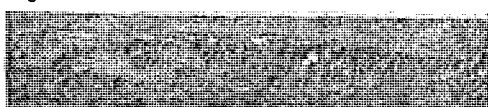
Fig. 12 — Severe Pitting of Sucker Rods

Fig. 13 — Sweet Pitting with Corrosion-Erosion   Fig. 14 — Corrosion-fatigue Cracks with no Visible Pitting
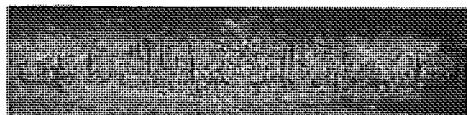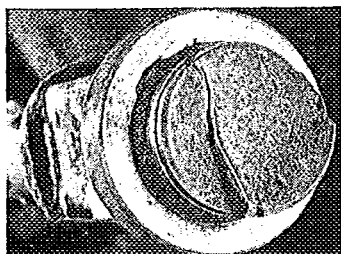
Fig. 15

Pin Break
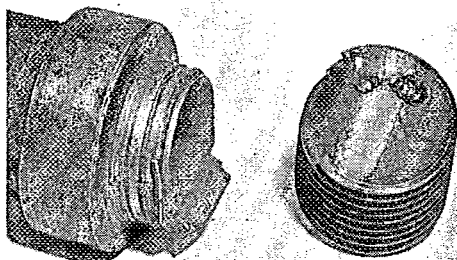
Fig. 16
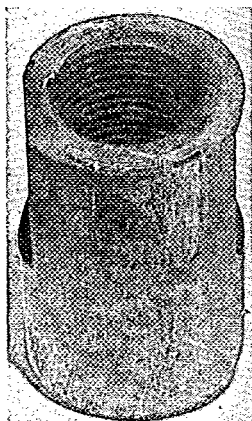
Fig. 17 (left) — Coupling-thread Break
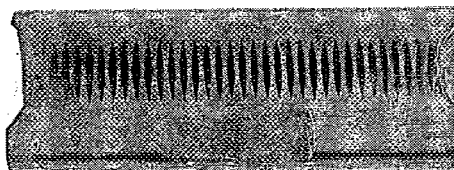
Fig. 18 (above) — Corrosion Wear of Coupling
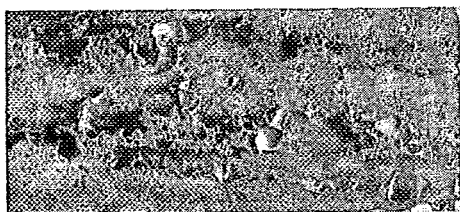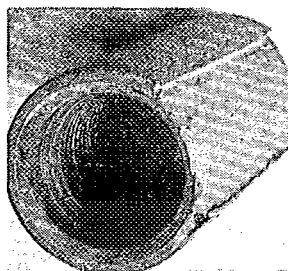
Fig. 19 — Severe Corrosion of Coupling
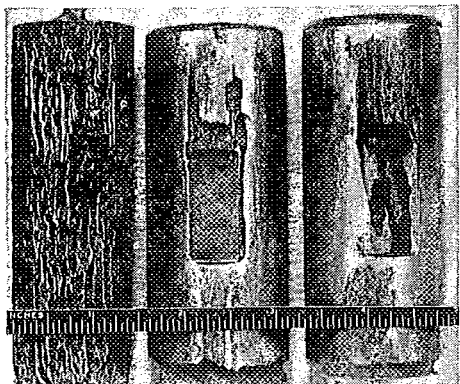
Fig. 20 — Upset Breaks

Fig. 19a — Corrosion of Alloy Coupling in Sweet Condensate Well
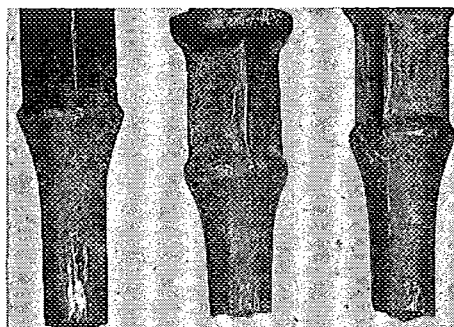
Fig. 21 — Corrosion-Erosion of Coupling

Fig. 22 — Corrosion-Erosion of Alloy Rod

Though the iron content of condensate waters varies widely, a survey by
the NGAA gave an average of 310 ppm* for corrosive wells and 125 ppm
for noncorrosive wells. In practice, many corrosive wells have as little as
100 ppm iron. It has been possible to reduce iron content of corrosive wells
to as low as 10 to 25 ppm by effective inhibition. In oil wells, iron content
of corrosive wells may range from 5 ppm up to several hundred parts per
million where large concentrations of iron are present in formation water.

The occasional failure of iron counts to correlate with corrosion failures
can best be explained by considering the types of attack. If the corrosion is
a uniform metal removal, the iron count can be high but the damage to
equipment relatively small. On the other hand, if the corrosion damage
results in deep pits, the iron count may be low but the damage severe.
Also, the amount of water produced has considerable bearing on the inter-
pretation of iron-content data. Obviously 5 ppm iron in 1,000 bbl of water
represents far more corrosion than 50 ppm in 10 bbl of water. To reduce

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Parts per million
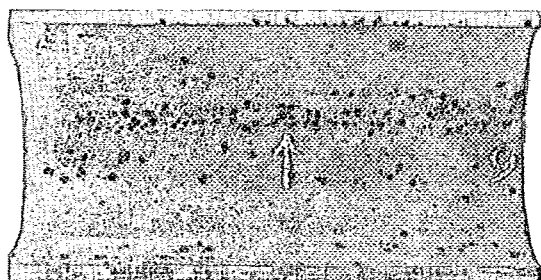
Fig. 23
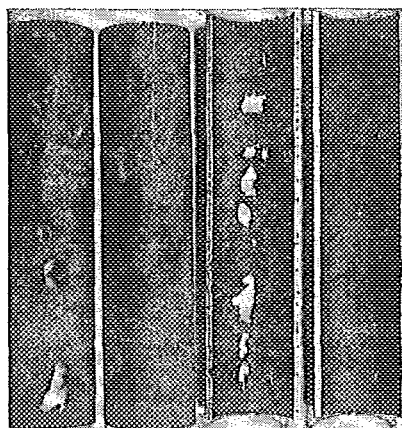
Fig. 24

Severe Pitting of Tubing in Sweet Oil Wells
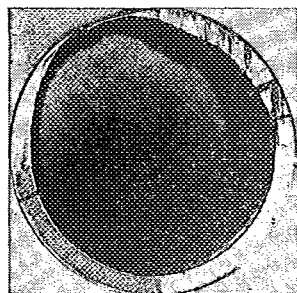
Fig. 25 (left) — Corrosion Wear
of Tubing
Wear all on one side—protective
scale intact on other.

Fig. 26 (right) — Corrosion Wear
of Tubing
Wear has been severe at several
points.
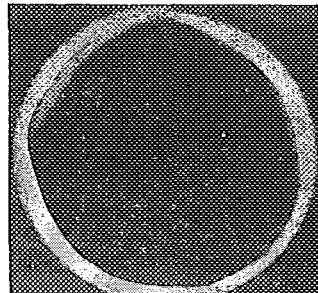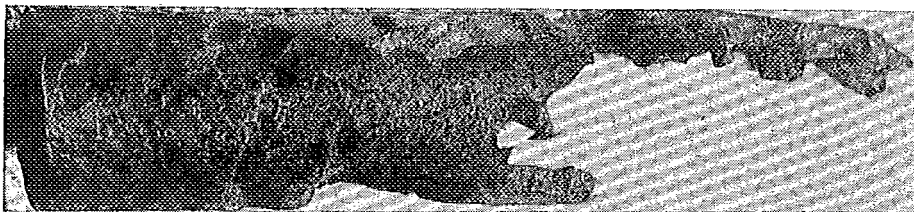
Fig. 27 — Equalizer Tube from a Gas-lift Valve

iron content to a comparative basis, the iron content is converted to pounds of iron being removed per day. In this instance, iron losses can be readily determined using the nomograph in Fig. 28. For example: With a ruler, draw a line from 5 ppm in Col. 1 to 1,000 bbl per day in Col. 3. This line intersects the middle column at 1.8 lb of iron removed per day. The principal value of iron analysis is not in predicting extent of corrosion, but in determining changes in corrosivity. For example, iron analyses are useful in showing increased corrosivity as water production increases, or for evaluating the effectiveness of inhibitors. Such data are shown in Fig. 29, which has been plotted from data for the North McCollum Field.

Iron-content data is no better than the technique used in obtaining and analyzing the sample and the analytical procedure. In all cases, samples should be taken from representative flowing fluids and not stagnant systems. Samples taken at the well head are usually superior to all others. In any case, the loss of iron can represent general or pitting corrosion. It is important to establish the extent to which variations in iron counts relate to corrosion rates in your field.

Corrosion Test Coupons

The corrosion test plate or "coupon" is another tool used to evaluate corrosion. The coupon is a small specimen of metal, usually low-carbon steel, which is exposed to the well fluids for 2- to 4-week periods. The loss in weight is used as a measure of corrosion and is reported as "mils per year" (mpy) penetration. This method of evaluation assumes that the corrosion is uniform, which may not be true because the loss in weight may be caused by pitting. The visual appearance and maximum pit depth of the coupon is usually reported along with the weight loss. The calculation of corrosion rates from coupon weight loss data is made according to the following equation:

$$mpy = \frac{\text{weight of metal removed (grams)} \times 1,000}{\text{specific gravity of metal} \times 16.387 \times \text{area} \times \text{years}}$$
$$\phantom{mpy = \frac{}{}}\text{(g/cc)} \quad \text{(cc/cu in.)} \quad \text{(sq in.)} \quad \text{(days/365)}$$

2. SWEET CORROSION   13

READ 1.8 LBS.
IRON REMOVED/DAY

READ 0.18 LBS.
IRON REMOVED/DAY

PPM IRON

LB. IRON
REMOVED / DAY

BARRELS
WATER / DAY
(42 GAL./BBL.)
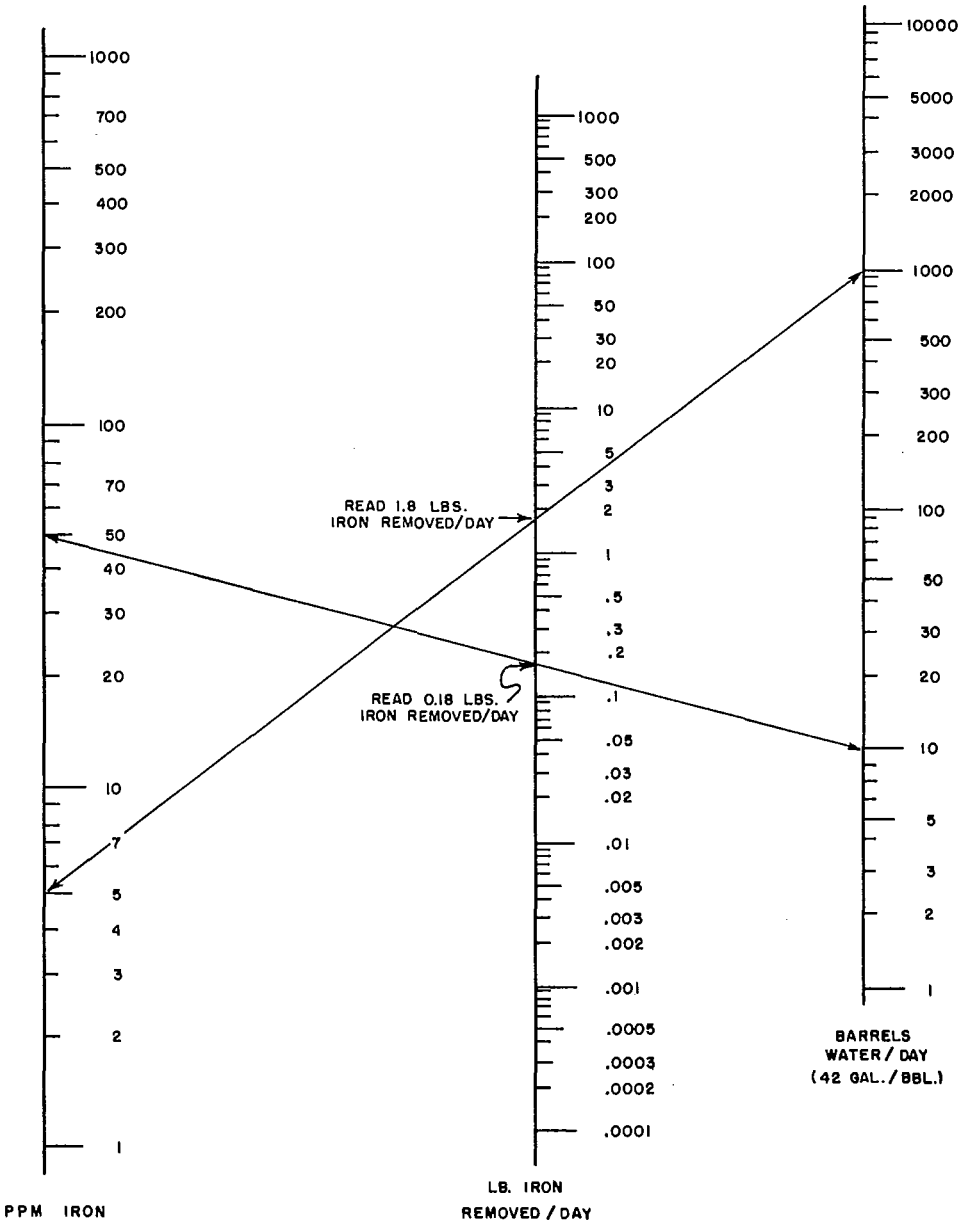
Fig. 28 — Iron-loss Nomograph
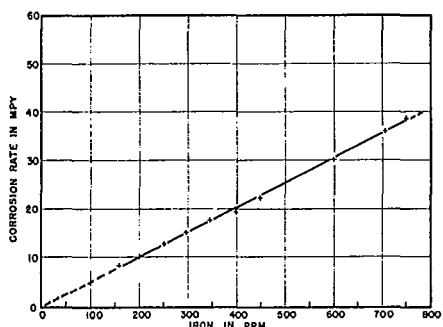
Fig. 29 — Correlation of Iron Content and Coupon
Corrosion Rate for North McCollum Field
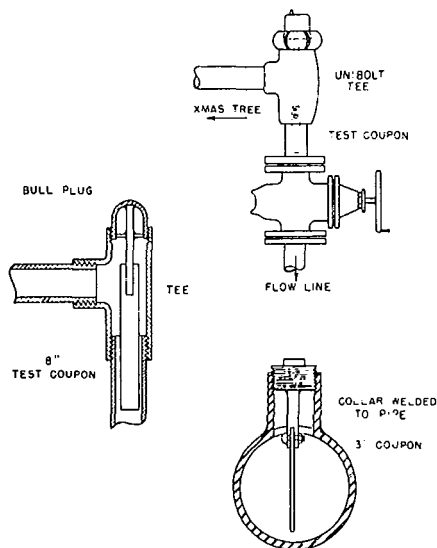
Fig. 30 — Typical Wellhead Coupon Installations
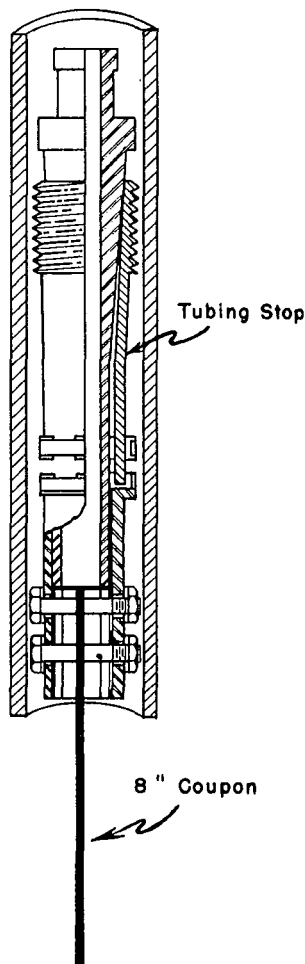
Fig. 31 — Wireline-operated Tubing Stop
Adapted as Downhole Coupon Holder

For a $1/16$ in. $\times$ 1-in. $\times$ 8-in. mild steel coupon:

$$\text{mpy} = \frac{\text{weight loss (grams)} \times 365 \times 1{,}000}{\text{days} \times 7.86 \times 16.387 \times 16.6}$$

$$= \frac{\text{weight loss (grams)} \times 365{,}000}{\text{days} \times 2{,}138.08}$$

$$\text{mpy} = \frac{\text{weight loss (grams)} \times 166}{\text{days}}$$

Typical wellhead coupon installations are shown in Fig. 30. In all cases, coupons should be electrically insulated from the wellheads or flowline by use of non-metallic holders.

One obvious limitation of coupons is that they indicate the corrosion rate only at the point of exposure. A number of operators have used sub-surface installations to obtain rates at various depths. This technique has proven to be valuable for special studies, but is too expensive for routine use. A downhole coupon installation which can be run using standard wireline equipment is as shown in Fig. 31. Typical data obtained using surface and downhole coupons are illustrated in Fig. 32.

Scale and paraffin depositions on the coupon can produce erroneous indications. These factors should be considered when evaluating a coupon survey. Also the fact that the corrosion rate indicated by the coupon is a relative figure, because corrosion may be affected by a combination of pressure, temperature and velocity, and it is very difficult to assure cou-pon placement in an exactly similar environment. Other factors affecting coupon results include: *1*, Coupon steel generally is not manufactured from the material in which it is being placed; *2*, If the metals are identical, the coupon is in the middle of the flow stream and may be damaged due to erosion; *3*, The coupon will be located in one phase of the production stream and may remain oil wet and therefore uncorroded.

Equipment Inspection

Caliper surveys are widely used as an index of corrosion. Within the limitations of the tool, the survey is a direct measurement of the damage that has occurred in the subsurface equipment. The tool, as shown in Fig. 33, consists of a number of peripheral feelers which bear against the inner surface of the pipe. The feelers actuate a stylus that records the greatest
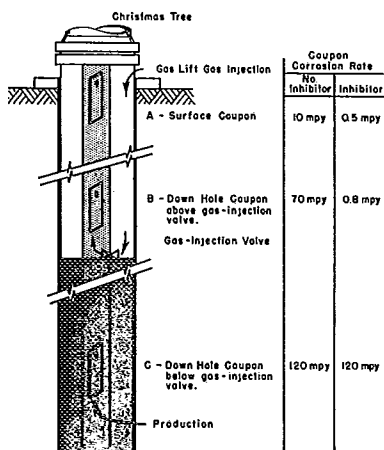
Fig. 32 — Coupon Installation in Well Produced by Gas-lift
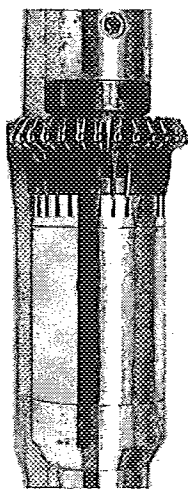
Fig. 33 — Feelers of Tubing Caliper
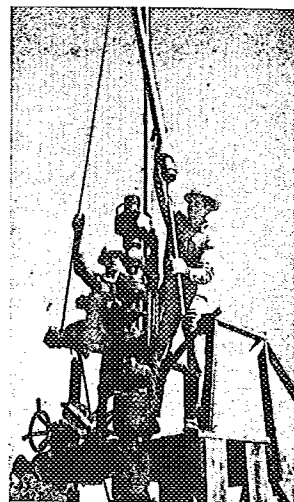
Fig. 33a — Lubrication of Tubing Caliper into High-pressure Well
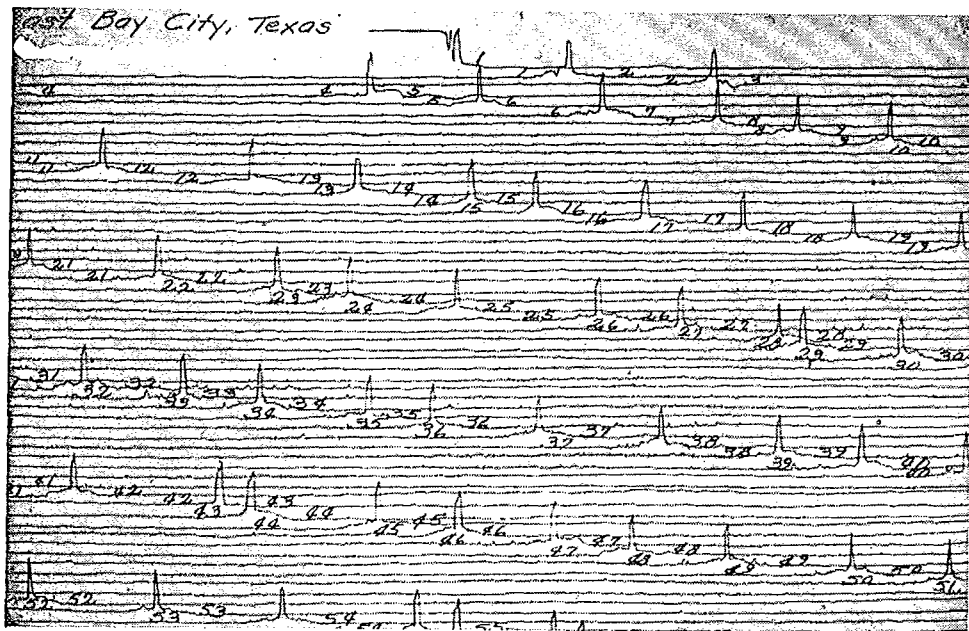
Fig. 34 — Caliper Survey Showing Corrosion in Early Stages
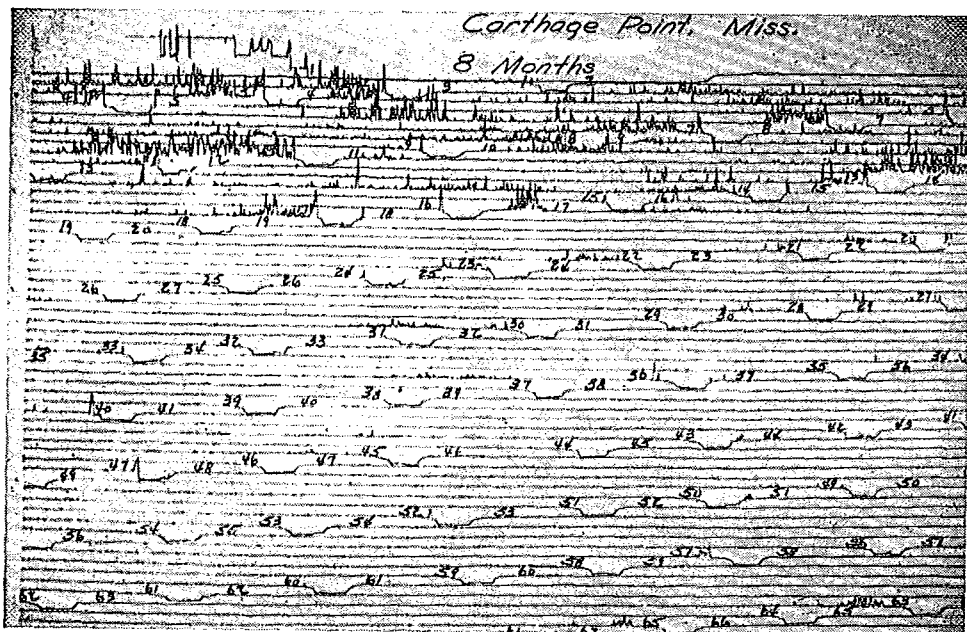
Fig. 35 — Caliper Survey Showing Severe Only above Zone of Water Condensation in
Condensate Well

pit depth at the location of the feelers. The possibility of the feelers missing some pits or only partly entering other pits must be considered. Also, scale or corrosion products can mask the true condition of the pipe. Usually, a consideration of pit depth and general condition of the pipe is a better approach than using a literal pit-by-pit interpretation. Caliper surveys are most valuable when they can be compared to a known condition (e.g., an earlier survey in the same well or new tubing). Several typical surveys are shown in Fig. 34 to 37, incl.

The use of caliper surveys in coated tubing is considered a poor practice. The feelers are hard metal and bear against the pipe with considerable force. Damage to the coating usually occurs at the end of the joint as the feelers spring out into the collar.

There is a real danger in running calipers in corrosive wells which will not subsequently be treated with inhibitors. Caliper feelers remove protective scales and allow corrosion to occur in the feeler tracks. A photograph of such a phenomenon is shown in Fig. 38 and 39.

The benefits obtained from a visual *equipment inspection* should not be overlooked. This procedure is most applicable to surface equipment and may indicate that a corrosive condition exists before equipment failures occur. This type of evaluation is especially useful in gas-condensate wells where corrosion is aggravated by turbulence. If coupon and iron-analysis data indicate corrosion, inspection of the equipment should be made.

Accurate records of equipment failures cannot be over-stressed as a means of evaluating a corrosion problem. If accurate records have been kept, many times a pattern of corrosion can be discovered before individual failures are sufficiently outstanding to indicate that a problem exists.

CONTROL MEASURES

Design and Operating Techniques

Design and operating techniques can be used to combat corrosion in two ways. The original design can be chosen: *1*, to reduce the severity of corrosion; and *2*, to allow mitigation procedures to be easily applied if corrosion appears in a well. Selection of tubing to reduce corrosion caused by high flow rates, designing the christmas tree and surface flow lines to reduce turbulence, and designing rod strings are all applications of this principle. Sometimes the water-oil ratio can be reduced by squeezing off water-bearing formations. Poor or questionable operating techniques can be the difference between success or failure of a mitigation program.

Corrosion Inhibitors

Corrosion inhibitors are used extensively in both oil and gas wells to reduce corrosion damage to subsurface equipment. Most of the inhibitors used in the oilfield are of the so-called "polar organic" type. All of the

18   Corrosion of Oil- and Gas-well Equipment
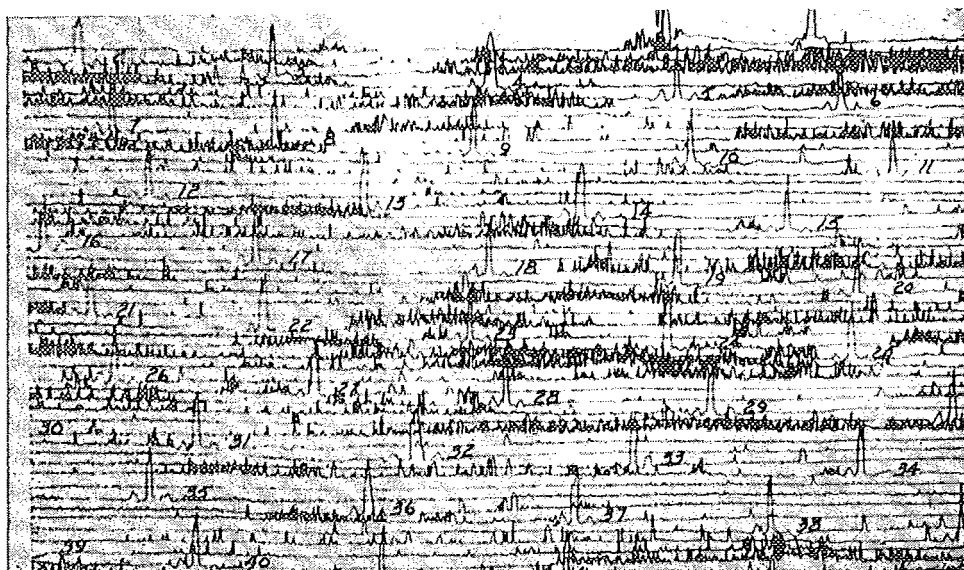
Fig. 36 — Caliper Survey Showing Severe General Corrosion
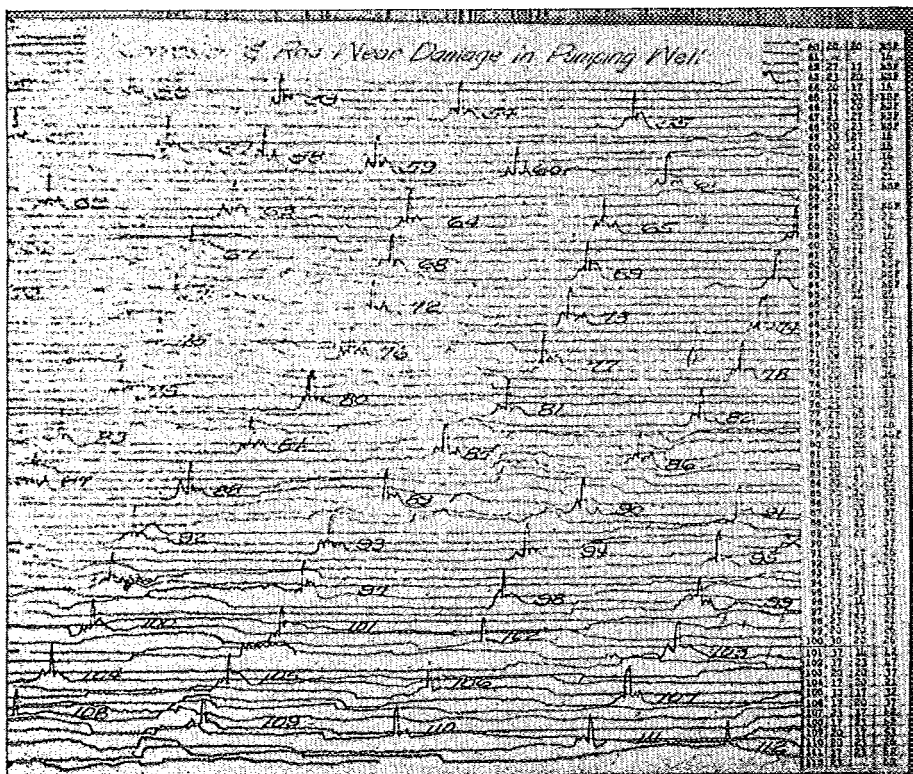
Fig. 37 — Caliper Survey Showing Erratic Pattern of Corrosion and Rod-wear Damage in Pumping Well

major inhibitor suppliers now can furnish effective inhibitors for the prevention of sweet corrosion as encountered in most fields. The major factors to be considered are the selection of the proper inhibitor and application procedure.

Wells, either flowing or pumping, completed without a packer are usually treated by dumping the chemical down the annulus so that it drops to the well bottom and enters the tubing with produced fluids (Fig. 40). The chemical is sometimes flushed down with the produced fluids. In some situations it has been most successful to use oil soluble inhibitors; in other cases, water soluble inhibitors. It is important to select the best inhibitor or evaluate the type of inhibitor for a given well. Inhibitor screening methods have been developed that are accurate and field proven. These methods are known as linear polarization and potentidyne. They have proven to be more accurate than the wheel test.

In gas lift wells there is a special problem of getting the inhibitor to drop below the operating gas lift valves. This results in protection of only that portion of the tubing above the lowest operating valve (Fig. 41).

Wells with the annulus packed off present an entirely different problem. Inhibitor cannot be injected into the annular space (Fig. 42). Methods that have been used for chemical protection in this type of completion include:

1. *Batch Method.* Alternative batch treating methods include pump and shut-in, pump and displace, and atomization. The choice of the method should be based on individual well characteristics.

2. *Continuous Injection Method.* There are four different methods available to perform this type of inhibition.

   a. *Continuous Injection Method.* One of the latest developments and preferred methods is injecting filtered inhibitor through a small diameter stainless or inconel encapsulated or bare tubing (Fig. 43) that is attached to the outside of the tubing string and is tied into the tubing string near the packer.

   b. *Gas Lift Injection.* Injection through a gas lift mandrel. The inhibitor is generally atomized into the gas that is utilized for gas lift. The inhibitor then travels through the annulus and enters the tubing string at the point of the mandrel (Fig. 41).

   c. *Treater Strings.* An extra string of tubing is run inside of the production tubing (Fig. 44) or as a separate dual string (Fig. 45). Inhibitor is injected into the annulus between the two tubing strings or down one of the dual strings and production is through the other string.

20   CORROSION OF OIL- AND GAS-WELL EQUIPMENT
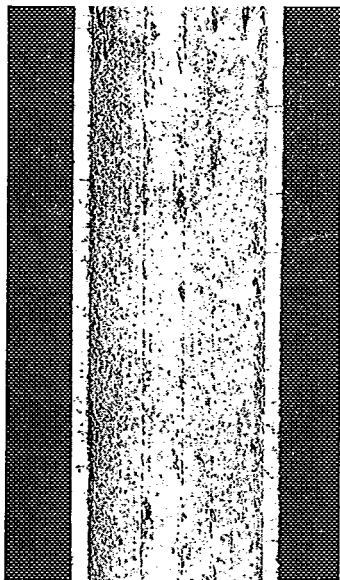
Fig. 38 — Corrosion in Caliper Feeler
Tracks of Uninhibited Well
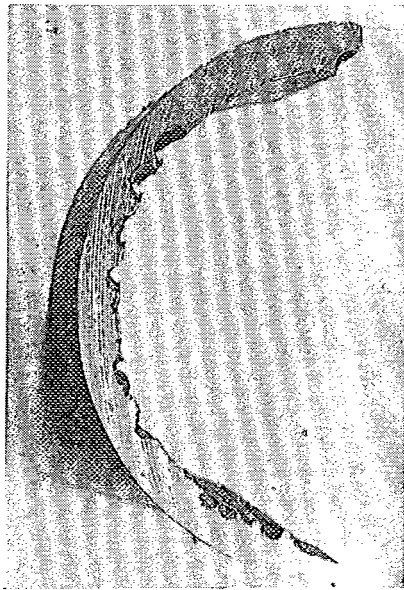
Fig. 39 — End View of Caliper Track Corrosion

Fig. 40 — Open Annulus (Packerless)
Completion

PRODUCTION
CASING

CORROSION
INHIBITOR

PRODUCTION
TUBING

PRODUCTION
TUBING

CORROSION
INHIBITOR

ANNULAR GAS
LIFT VALVE

CASING

TUBING

PACKER

PRODUCTION
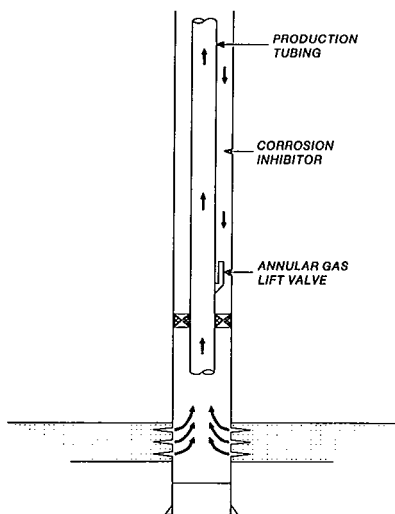
Fig. 41 — Annular Gas-lift Valve Completion
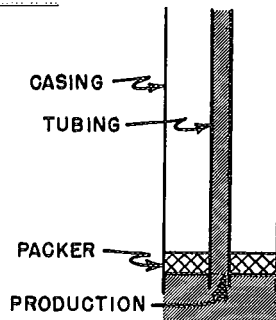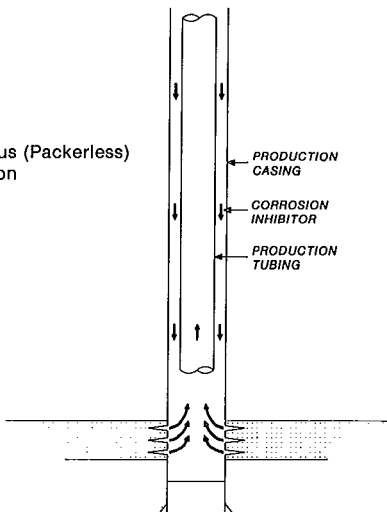
Fig. 42 — Packed-off Well
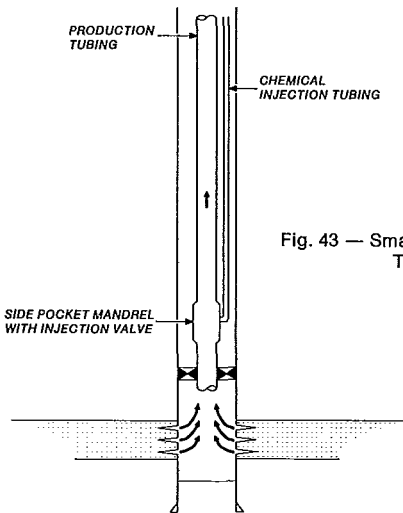
Fig. 43 — Small Diameter Chemical Injection
Tubing Completion

Fig. 44 — Concentric Completion
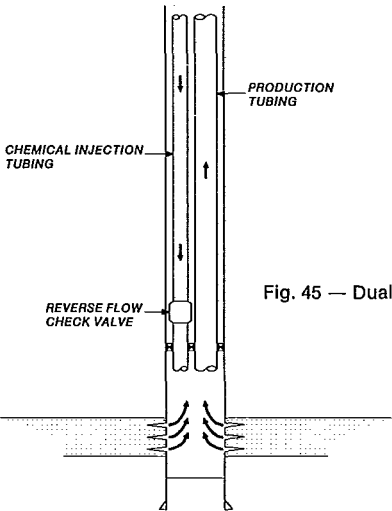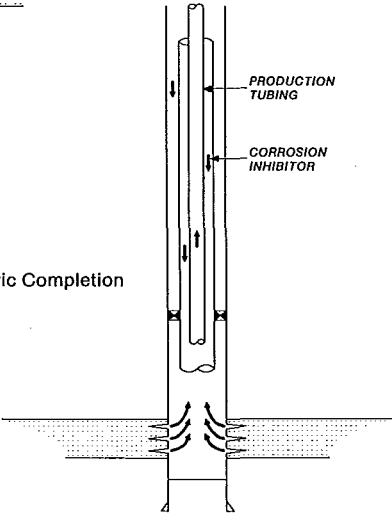
Fig. 45 — Dual Completion
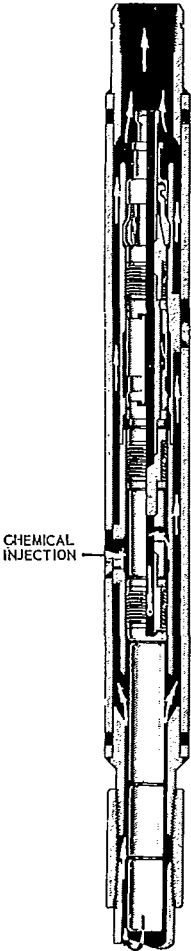
Fig. 46 — Bottom-hole —
Bypass Chemical
Injection Valve

    d. *Injection Valve.* A bypass chemical injector valve (Fig. 46) is run in the tubing string just above the packer. The annulus is filled with inhibitor and pressure applied on the annulus forces the inhibitor through this valve into the tubing.

3. *Squeeze Method.* Inject large quantities of inhibitor down the tubing into the formation. Inhibitor then is produced with the production fluids and inhibits the tubing. Extreme caution should be exercised when using this method. The inhibitor selected may not be compatible with the sands or clays in the reservoir and could cause irreversible damage. The compatibility problem should be evaluated prior to final selection of an inhibitor.

Alloys

Although the use of inhibitors is the most common method of corrosion control in condensate wells, alloys are also used. Nine-percent nickel steel was used for tubing until a few years service showed that these alloys were subject to stress-corrosion cracking. Twelve-percent chromium steel tubing is being used where inhibition is difficult, but still may not afford the needed protection without the use of inhibitors. The use of all high strength tubing is fraught with difficulty because of mechanical properties. A major problem in the use of high strength tubing is the decrease in ductility with increase in strength.

In miscellaneous wellhead equipment alloys are quite generally used. Choke bodies are made of 12-percent chromium steel. Ring joints, choke beans, valves, and thermometer wells are made of the stainless steels and of brass, bronze, and Monel*. The selection of alloy material requires serious consideration of the environment and conditions under which it is used. High velocity and sand production can make even 12-percent chromium alloys insufficient to prevent corrosion damage.

Protective Coatings

Protective coatings are a time honored and obvious way of preventing corrosion. There is no problem in finding coatings with sufficient corrosion resistance. The major problem is in getting an application of coating which is free from pin holes and in getting joints properly coated. Coatings must be handled with care. Running wireline tools in coated tubing can damage the coating and should be avoided, unless necessary.

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*Monel is the International Nickel Company's registered trademark for an alloy of approximately 2/3 nickel and 1/3 copper.

CHAPTER 3

SOUR CORROSION

A large percentage of the wells in this country are producing hydrogen sulfide and many are corrosive. In the absence of protective measures, hydrogen sulfide corrosion in these corrosive sour wells costs hundreds of dollars per well per month for equipment failure. This figure varies, of course, depending upon individual well conditions. There are records of this type of corrosion costing in the thousand dollar range per well per month. From these figures it can be readily seen that the cost of replacing equipment alone could be well into the millions of dollars per year for the industry.

Sulfide corrosion generally starts slowly and the rate increases with time. Chemical inhibition, coatings, and, in some cases, special alloys have been used to successfully combat this attack. The favorable economics of corrosion mitigation have been proven by most operators, and corrosion-control methods are standard practice in field operations.

DESCRIPTION OF DAMAGE

Chemistry of Reaction

Although hydrogen sulfide is noncorrosive in the absence of moisture, if moisture is present the gas becomes corrosive. It becomes very severely corrosive where even a trace level of oxygen (O_2) is present, and also may be influenced by a significant presence of carbon dioxide (CO_2). The general mechanism of this type of corrosion can be simply though not completely stated chemically as follows:

$$H_2S + Fe + H_2O \longrightarrow FeS_x + 2H$$

Hydrogen sulfide	Iron	Water	Iron sulfide	Hydrogen
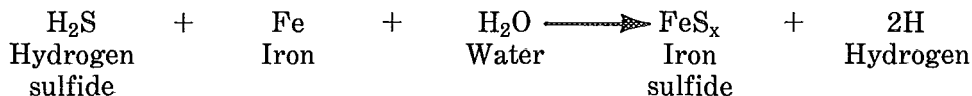
Though iron is used in this example, other metals react in essentially the same manner to produce metallic sulfides. The iron sulfide produced by this reaction generally adheres to the steel surfaces as a black powder or scale. The scale tends to cause a local acceleration of corrosion because the iron sulfide is cathodic to the steel. This reaction results in deep pitting noted on equipment as shown in Fig. 47.

Another reaction occurs with hydrogen sulfide corrosion. The hydrogen released in the foregoing reaction enters into the steel where it is absorbed into the steel and embrittles it. It may also form molecular hydrogen which leads to *blisters* and *cracks* (Fig. 48 and 49).

As seen in the foregoing equation for the corrosion reaction, neither oxygen nor carbon dioxide is required to produce sulfide corrosion. Their

Fig. 47 — Deep Pitting of Sucker Rod in Sour Service
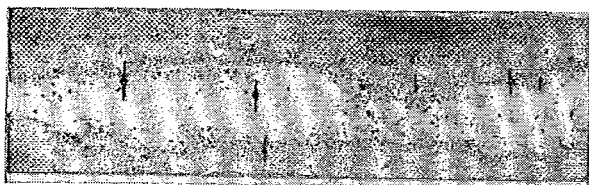
Fig. 49 — Cracks Due to H₂S Originate in Tiny Pits
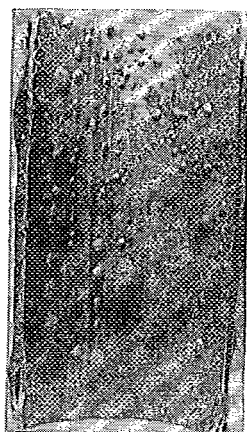
Fig. 48 — Blistering Due to H₂S

presence, however, greatly accelerates the severity of sour corrosion. In fact, one of these is always present where hydrogen sulfide corrosion is a severe problem.

It has been shown by various investigators that micro-organisms can greatly affect corrosion rates. In order for micro-organisms to accelerate corrosion, the environment must be suitable for their growth and multiplication. Moisture, essential minerals, organic matter, an energy source, and a suitable pH must be provided. In many cases, when steel structures are in contact with the earth or water, all the necessary requirements are met. It is, therefore, not surprising that microbiological corrosion is quite common.

Micro-organisms such as the Desulfovibrio (sulfate reducers) can cause sulfide corrosion in the absence of atmospheric oxygen (anaerobic conditions). These organisms utilize hydrogen formed by electrochemical corrosion during their growth and reduce sulfate (SO_4) to H_2S. Both hydrogen utilization and H_2S formation cause increased corrosion rates.

Oil-well Tubing

In oil-well tubing water droplets break out of the oil and wet the surface of the tubing. The hydrogen sulfide dissolves in these droplets and causes the development of pits. On surfaces such as the inside of tubing and rods, where the flow of fluid gives erosion effects, the pits are generally smooth and appear as depressions (Fig. 50). Another major cause of tubing corrosion is corrosion-erosion or what is commonly called "box wear" or "rod wear" (Fig. 51).

Annular-space Corrosion

On the exterior of tubing or the interior of casing above the annular-fluid level where no erosion effects are in operation, the pits may have sharp edges and be cavernous (Fig. 52).

3. SOUR CORROSION   25

Fig. 50 (left) — Sour Oil-well Tubing Corrosion

Fig. 51 (right) — Corrosion Wear of Tubing in a
Sour Pumping Well
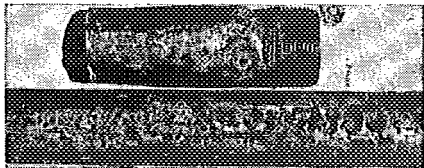
Fig. 52 (above) — Cavernous-type Pitting in
Annular Space — Exterior Tubing

Fig. 54 (above) — Internally Corroded 5½-in.
Casing
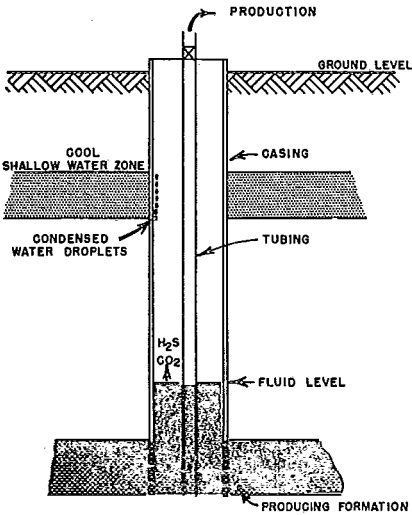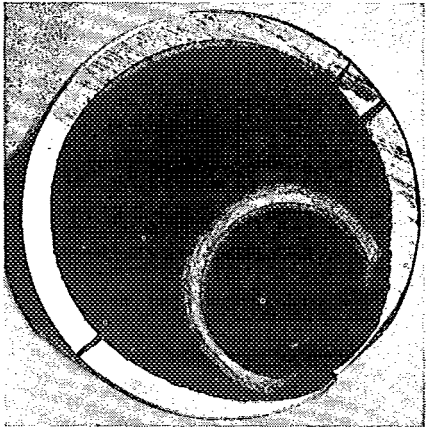
Fig. 53 (above) — Internal Casing Corrosion
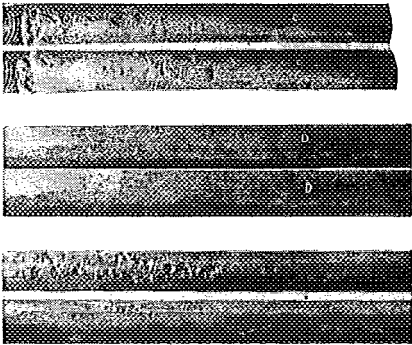
Fig. 55 (above) — External Tubing Corrosion
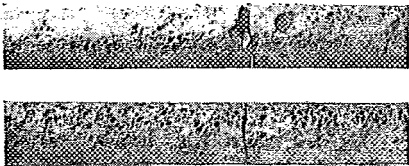
Fig. 56 (left) — Sour Pitting of Sucker Rod
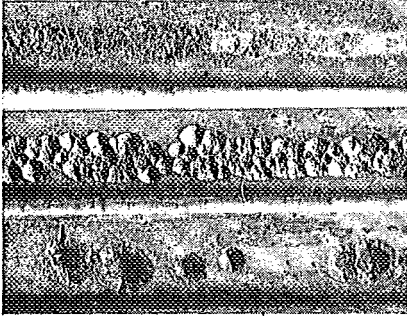
Fig. 57 (above) — Pitting of Sucker Rod in Sour Service

Fig. 60 (above) — Top Rod Was 3½-percent Nickel Steel, Lower Rod a Low-alloy Pearlitic Rod

Despite the greater pitting, the pearlitic rod gave longer service.

Fig. 62 (above) — Severe Corrosion of Pin End
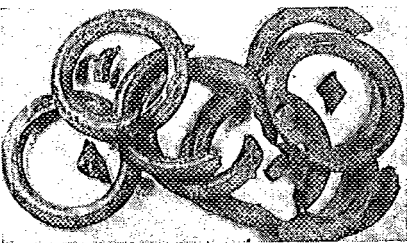
Fig. 64 (above) — Embrittled Relief Spring Exposed to Sour Condensate

Fig. 65 (right) — Corrosive Zones in Sour Crude Storage Tanks

Fig. 58 (above) — Cracks Originating in Series of Sharp Pits

Fig. 59 (above) — Few Cracks Originating in Broad Pits
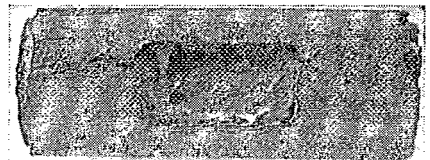
Fig. 61 (above) — Severe Corrosion of Uncarburized Area of Coupling

Fig. 63 (right) — Sulfide Corrosion of Sucker Rod Caused Minute Pit at Top

Crack begins at base of pit. Jagged area of bottom shows tensile break.

AIR IN AS TANK BREATHS

CONDENSED MOISTURE

VERY SEVERE CORROSION DUE TO BREATHING OF AIR AND CONDENSATION OF MOISTURE

VAPOR SPACE

H₂S BOILS OUT

OIL

MILD CORROSION WHERE OIL CONTACTS WALLS

SALT WATER

CHUNKS OF IRON SULFIDE

BRINE CAUSES CORROSION
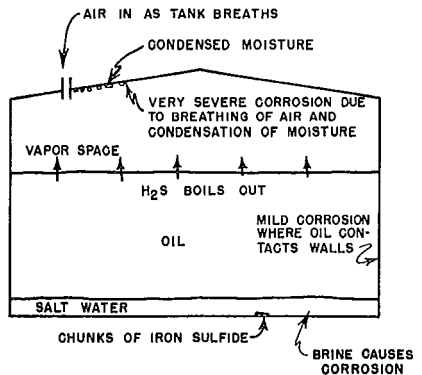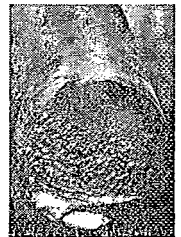
In the interior of oil-well casing, the mchanism of attack by hydrogen sulfide is as follows: In the absence of a packer, the casing-tubing annulus is exposed to the reservoir gases. The gas is saturated with water at reservoir conditions. As the gas diffuses up the hole, the water condenses on the surface of the casing at areas which are cooled below the dew point (Fig. 53). Hydrogen sulfide then dissolves in the water droplet and corrosion is initiated. Because there is little or no flow in the annulus, the iron sulfide scale is not removed. This scale encourages pitting, as mentioned earlier. A section of internally corroded casing is shown in Fig. 54.

In many cases, the external surface of the tubing does not show the effects of hydrogen sulfide corrosion. The lack of corrosion of the tubing is believed to be the result of its high temperature as compared with that of the casing. The flow of production through the tubing can raise the temperature of the tubing surfaces above the dew point of the gas in the annulus. If this happens, no condensation of the water will occur and, as a result, the external tubing surfaces will be free from attack. In cases where tubing exterior is corroded it may resemble Fig. 55.

Sucker Rods

Sulfide corrosion on carbon-steel sucker rods usually appears as smooth pitting (Fig. 56). Small fatigue cracks may be at the base of these pits. Similar cracks form at areas of surface damage, such as wrench marks, even when corrosion attack is negligible. This cracking is caused by stress concentrations developed at the base of the pit and by embrittlement resulting from sulfide attack. Some embrittlement can be expected in sour systems. Several examples of rod failure are shown in Fig. 57 through 62.

Examination of the broken end of a sucker rod that has failed in service generally reveals a smooth surface extending over approximately one half of the breakage plane. The remaining section will show a tensile break with a jagged edge where final parting occurred. Evidence of the initial cracking can often be found on the side opposite this jagged edge (Fig. 63). The small initial crack was extended across the rod in gradual stages and the cracking was aided by the corrosion. Failures of this type are described as corrosion-fatigue failures.

Gas Wells

In certain gas wells very little, if any, pitting attack may be visible on the surface of the equipment, yet rapid failure of the equipment occurs. Failures of this type are attributed to sulfide stress cracking or hydrogen embrittlement. A striking example is the broken remains of a relief spring (Fig. 64).

Surface Equipment

Surface equipment handling sour production will, with few exceptions, exhibit the same type of attack as the subsurface equipment. In oil-storage

tanks and other equipment handling this type of production, where oxygen is present, sulfide corrosion can be very severe and rapid. Several distinctly different corrosion types are found (see Fig. 65).

In oil storage tanks, the corrosion on the underside of the deck starts from a combination sulfide and oxygen attack. This attack will, by itself, result in extensive pitting and can perforate the tank deck. A second type of attack occurs on the bottoms of storage tanks. This corrosion is the result of the water layer which is generally found on the bottom of all tanks. This sulfide saturated water sets up corrosion which proceeds rapidly and results in perforation of the tank bottom. A secondary reaction occurs in tank bottoms which is caused by the heavy corrosion scales dropping from the underside of tank decks. These large chunks of scale fall to the bottom of the tank where they cause concentration cell attack resulting in severe pitting. Corrosion of the shells of tanks is normally negligible. However, severe attack has been noted in the bottom 18 in. at the oil-water interface. Sometimes severe hydrogen blistering is a major storage-tank problem (Fig. 66).

Injection Equipment

Injection equipment for water or gas injection can be expected to show, in general, the same corrosion as comparable production equipment. In the case of water injection, a higher corrosion rate can be expected because of possible oxygen contamination through surface handling. A sample of very severe corrosion of pipe exposed for 18 months in an injection well is shown in Fig. 67. Equipment handling water from supposedly sweet production has been found to suffer severe corrosion from microbiological attack. In some cases, the H_2S produced by biological activity can be detected only as an iron sulfide corrosion product. An added problem is the plugging of injection wells by iron sulfide and iron oxide corrosion products.

Fig. 67 — Very Severe Corrosion of Injection-well Tubing

Fig. 66 — Hydrogen Blistering on Sour Crude Storage Tank

METHODS OF EVALUATING THE PROBLEM

Analysis of Produced Fluids and Gas

When a corrosion failure occurs in equipment handling sour produc-
tion, the damage can generally be attributed at least in part to hydrogen
sulfide attack. However, no exact correlation of corrosion with the amount
of H_2S, CO_2, or water production has been obtained. Analysis of produced
fluids will show whether hydrogen sulfide is present. Experience has
shown that traces of H_2S are present in many "sweet" wells and react so
rapidly with either dissolved iron in the water or the well's equipment that
none is detectable in the production. An increasing number of cases are
being found where iron sulfide in tubing scale is the only indication of
sulfide.

The presence of black iron sulfide in the brine or as a scale on the
equipment is positive evidence of sulfide corrosion. Because of the adher-
ent, insoluble nature of the scale, the extent of corrosion cannot be accu-
rately evaluated by quantitative determination of the iron sulfide. When
oil wetted, iron sulfide has been shown to concentrate at the oil-water
interface. Iron tests on the produced oil and water may be of minor value
if enough tests can be taken on a given well to arrive at some statistical
analysis of data. Generally, this method is too time-consuming and costly
to be of appreciable value to the field in determining corrosion rates in
sour wells. Unless the corroding equipment is subjected to high velocity
fluid flow, some scale can be found on the metal surfaces. The scale may
vary from tiny spots in the pits to continuous layers ⅛ in. or more thick.
Detection of the scale may be hindered by the presence of oil and other
material and by rapid oxidation when the scale is exposed to air.

Calipers

Because of the insoluble nature of the corrosion products, the use of
mechanical calipers to determine the extent and degree of corrosion does
not give accurate results. The caliper may not be able to dislodge the scale
and the record shows no corrosion. Other times, only a fraction on the true
pit depth is indicated. Some operators run a wire brush ahead of the
caliper to remove loose scale, thereby increasing the accuracy of the tool.
It is generally understood that the log obtained with such a caliper is
optimistic and more of a qualitative than a quantitative indication of cor-
rosion. Calipers can be used to record reduction in wall thickness resulting
from box wear.

Coupons

Wellhead coupons have been used in obtaining qualitative indications of
corrosion rates. As a general rule, the surface coupons installed as shown
in the manner described in Chapter 2 do not represent actual conditions of
corrosion under subsurface conditions. Quantitative data from coupon
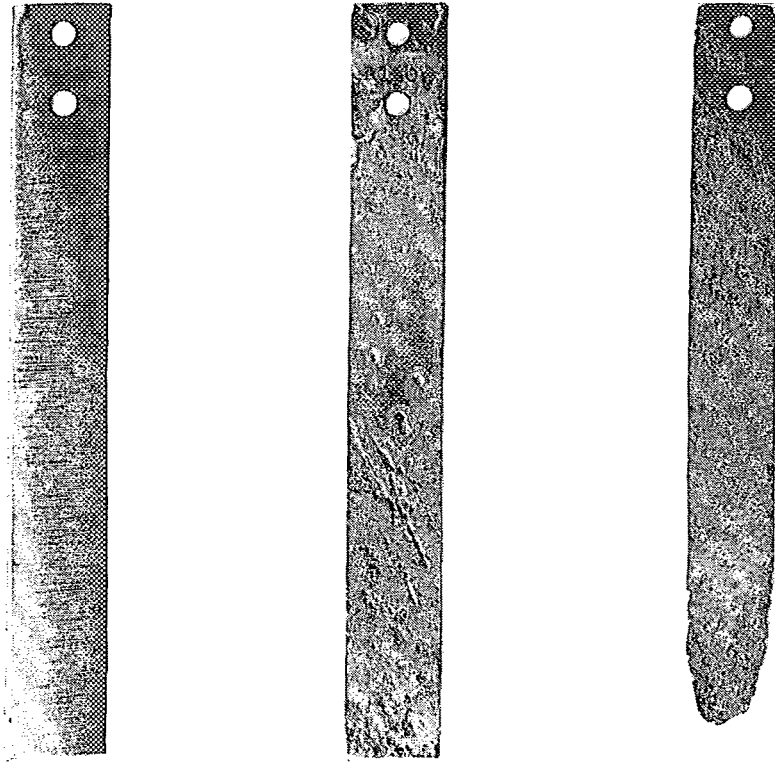
Polished unexposed coupon   Severe pitting corrosion from   Severe general corrosion in sour
                         salt-water disposal pit   oil well

Fig. 68 — Coupons

exposure are difficult to obtain, partly because of lack of representative wetting of the coupon. Coupons do, however, give indication that corrosion may be occurring (Fig. 68). The use of calibrated rod and tubing subs, or bottom hole coupons has proved more effective in determining downhole corrosion rates. Also, the use of calibrated test nipples has proven very accurate in determining internal corrosion rates on surface lines.

Equipment failure Records

Another method to determine the extent and severity of corrosion is use of equipment failure records. Records similar to that shown in Fig. 69 are very helpful in determining not only the amount but the cost of corrosion, both before and after treatment. In all cases, reduced pulling costs are the proof of effective corrosion control programs. Therefore, equipment failure records are extremely important in determining extent of corrosion and efficiency of a corrosion control program. Equipment failure records cannot be used to predict corrosion because the results of corrosion must be available to obtain failure records. Production and equipment performance

ANALYSIS OF WELL SERVICING AND SUBSURFACE EQUIPMENT FAILURES

POOL___DEEP POOL___
LEASE_____STATE_____
WELL NO. ____1____
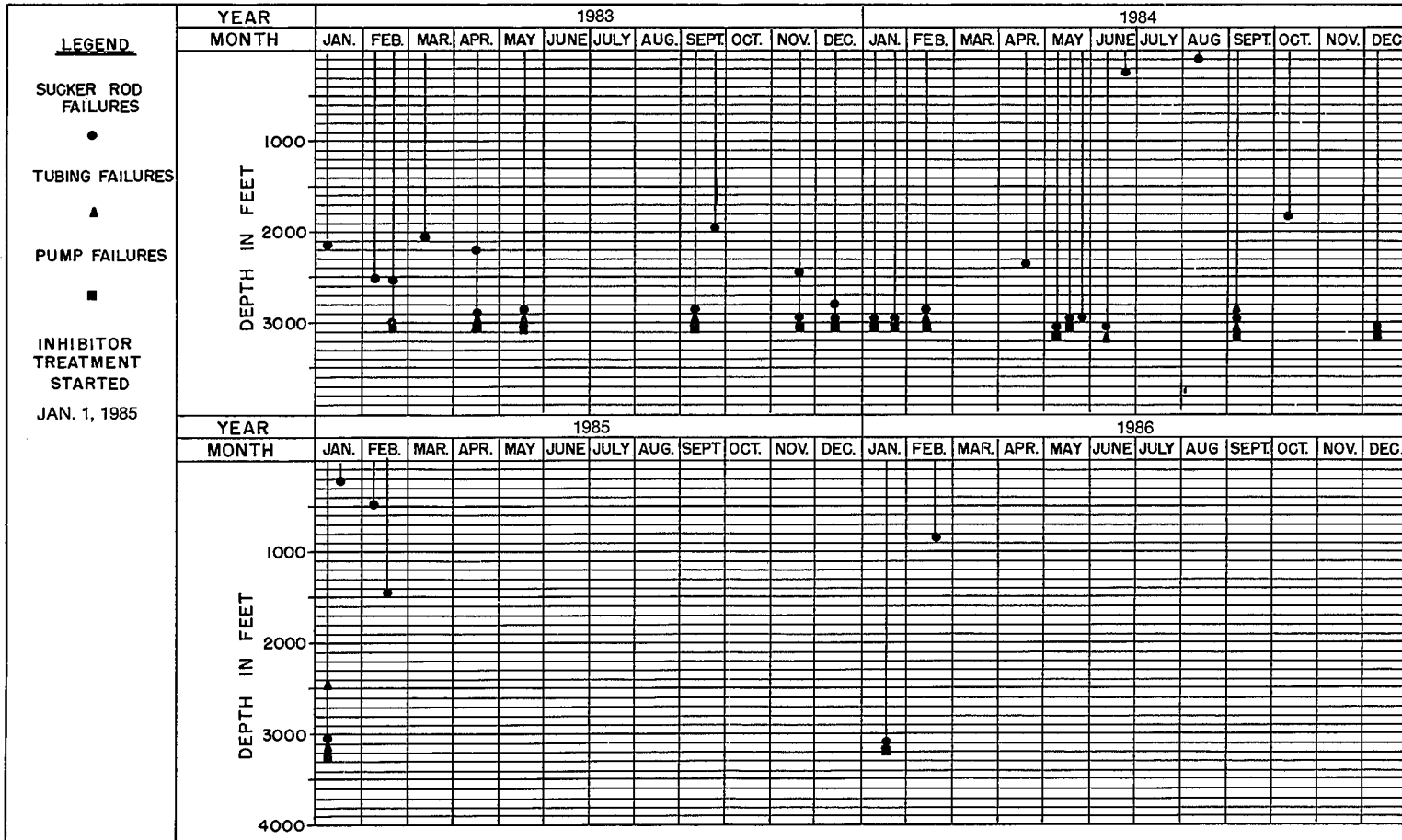
Fig. 69 — Record of Rod, Tubing, and Pump Failures in Typical Arbuckle, Kansas, Field

data are extremely important in determining the field's corrosion problems. Also, the results of careful examination of the failed equipment should be a part of these records.

CONTROL MEASURES

Design and Operating Techniques

The design of a system and operating techniques can greatly affect the corrosion which may be expected. In flow lines, the velocities should be kept high in order to prevent buildup of scale, but not high enough to cause erosion. All blind ends or obstructions which could serve as traps for scale should be eliminated. In gas lines, all low spots should be equipped with adequate means for removing any water which might collect.

The use of packer fluids and/or inhibitors are effective ways to prevent attack in the annulus. If the water production can be shut off, normally a reduction in corrosion rate will occur. Designing equipment to operate well within its physical limits will generally increase its life many-fold.

In vessels handling sour production, such as oil tanks, a cone shaped bottom with means of water removal has been successful in reducing bottom corrrosion. Monel sumps are often desirable. Water handling vessels should be designed so that the flow pattern does not leave "dead" areas where scale can accumulate.

Inhibition

Probably the most widely used method of controlling sulfide corrosion in subsurface equipment is by chemical inhibition. Because corrosion is a surface reaction, any modification of the steel-environment interface will affect the rate of corrosion. Certain chemicals which, when added to a corrosive system, modify this interface to reduce the corrosion rate, are called inhibitors.

Most of these compounds can be considered as functioning by adsorbing on the metal surface to form oil wet films. A very simplified visualization of this mechanism is given in Fig. 70. Generally, these materials have a very active polar group on one end of the molecule and an oil soluble tail. The polar group adsorbs to the equipment surface and arranges itself in such a manner that the oil soluble portions extend into the fluid flow. This oil soluble tail causes formation on the surface of an oil film and prevents water from contacting the steel, thereby preventing corrosion. Certain compounds have been proposed for use which are totally water soluble. These materials generally function by film formation, causing either a water-repellent film to form on the metal or a chemical film which is impervious to the corrosive agent.

3. Sour Corrosion   33

OIL FILM
WATER
OIL SOLUBLE END OF MOLECULE
POLAR GROUP
METAL SURFACE
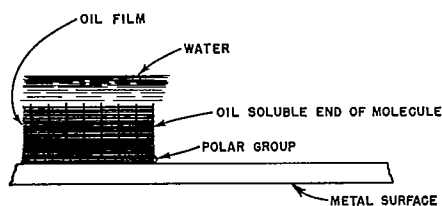
Fig. 70 (above) — Inibitor Mechanism
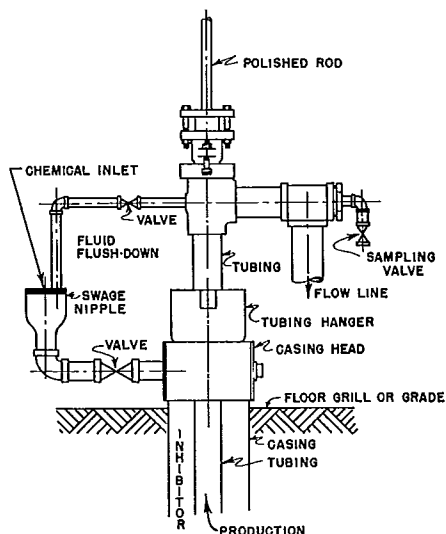
Fig. 71 (right) — Inhibitor Injection

POLISHED ROD
CHEMICAL INLET
VALVE
FLUID FLUSH-DOWN
TUBING
SAMPLING VALVE
FLOW LINE
SWAGE NIPPLE
TUBING HANGER
VALVE
CASING HEAD
FLOOR GRILL OR GRADE
CASING
TUBING
INHIBITOR
PRODUCTION

Inhibitors are generally lubricated down the casing at intervals determined by field testing. Fig. 71 shows an example hookup for inhibitor injection. It is generally good practice to thoroughly flush the inhibitor down the hole with large volumes of produced fluids. Considerable success has been obtained by using infrequent injections (e.g., once a week) of large volumes of inhibitor rather than daily injections of smaller amounts. Treating trucks capable of pumping inhibitor and produced water flush down the annulus are commonly used.

When using inhibitors, two important factors must be considered, viz., *1*, film formation; and *2*, repair of inhibitor film. The inhibitor films are seldom perfect and deteriorate because of abrasion and other factors. For this reason, repeated additions of the inhibitor to the system are required in order to maintain the film and obtain protection.

Flow line coupons are useful in determining the effectiveness of the inhibitor. However, a coupon only shows corrosion rates for the system at the point of exposure. Another effective method for checking corrosion rates is using iron counts from water analysis. The following is an example of how this is accomplished.

FC   = Fixed Constant (11.94)

Fe   = Dissolved iron (ppm by volume)

MD   = Measured Depth (feet)

ID   = Inside Diameter (inches)

BWPD = Barrels of Water Per Day

MPY   = Mils Per Year (thousands of an inch)

$$MPY = \frac{(FC)\ (Fe)\ (BWPD)}{(MD)\ (ID)}$$

A third method is the use of calibrated rod and tubing subs. The results from these methods should be checked against actual equipment life to determine the best method for each particular field.

The use of inhibitors for downhole corrosion has proven very economical. In some cases, savings in cost of replaced equipment of thousands of dollars per well per month have been realized. Inhibitors have been very effective in controlling rod and tubing corrosion and the use of volatile organic amine inhibitors has been effective in the control of internal vapor corrosion in casing. The life of subsurface pumps has been increased by the use of inhibitors, although the success has not been as outstanding as in the case of tubing and rods.

Alloys

In certain cases, some higher alloy steels and other metals and their alloys have proven very useful in preventing sulfide attack. Monel and other high-nickel alloys have proven economical in subsurface pumps under sour conditions.

It is well-established that the harder steels have a greater tendency toward sulfide cracking. In fact, steels harder than Rockwell C-22 should not be used under severe conditions.

The use of sucker-rod strings made up of different alloys is an excellent method for determining which material is most suitable for a given exposure. This mixed-string testing is also suitable for selecting which of the low alloys would be most resistant in a given well or which heat treatment would give best service in a given condition *(API RP 11BR: Recommended Practice for Care and Handling of Sucker Rods).*

Non-metallic Materials

Fiberglass sucker rods and similar plastic tubing, tanks, and line pipe have proven effective in some cases. Vinyl copolymers, epoxy, acetate butyrate, and other resins with and without glass reinforcement have been used. Although these materials have proven resistant to corrosion attack, the lack of complete design data has limited their use.

The use of structural plastics, either reinforced or non-reinforced, requires careful engineering analysis. Some of these materials exhibit excessive cold flow or long-term creep which limits their usefulness. In general, careful consideration must be given to temperatures and pressures to which the plastic installation is exposed. In plastic lines, the depth

of backfill must be considered as to its effect on causing the plastic to deform. Also, several of these materials are flammable and this aspect should be considered when designing plastic installations. Installations have been successful for several years, where properly installed.

Protective coatings have been used for interior coating for tubing, lines, tanks, and other vessels with varying results. Considerable use of these materials has been made in flood- and injection-water systems. Coal tar, both hot- and cold-type coating, has been used as tank coating for many years. This material has given spotty but generally good results depending upon the type of crude to which it was exposed. Epoxy, epoxy phenolics and nylons also have been used successfully for internal coating of tubulars and tanks.

Coatings based on vinyl copolymers have been extensively used since 1944. The coatings are permeable to hydrogen sulfide; and unless a lead pigment is used in their formulation or a lead primer is incorporated in the system, early failure will result.

Although the greatest use of coatings has been in tankage, salt water handling vessels, and line pipe, coated tubing for flowing and disposal wells has also been used. The use of coated tubing is, however, not widely accepted as a corrosion-control method for producing wells. Although a number of pumping wells have had coated tubing, the rubbing action of the rods has accelerated failure of the coatings.

The use of all surface coatings requires good surface preparation plus very careful application. More details on this subject are given in Chapter 4, Oxygen Corrosion. The use of wash primers and inhibitive primers should be carefully considered in any coating system. Careful inspection during application to maintain proper coating procedures cannot be over-stressed. Shop application of coatings is generally preferred to field applications, although this is not always feasible. Internal coating of pipe in place has been successful in increasing the life of pipelines.

Cement linings are used for piping handling sour brine. Cement linings have considerable limitations which must be considered when planning their use. Cement linings may be affected by acidizing. This is particularly important in water-flood and water disposal installations where scaling can be a problem. Normally, cement linings are permeable to water. This, in time, will allow a thin film of corrosion products to form between the lining and the substrata metal. This buildup of corrosion products can eventually lead to cracking and sloughing of the lining.

As most cement lining is shop-applied, the wall at the joint is vulnerable to poor installation practices and may be bare. Therefore, corrosion can start at that point and lead to rapid sloughing of the lining and failure of the pipe.

Cement-asbestos pipe has been useful in certain locations; however, the use of products containing asbestos has been severely curtailed. Reinforced plastic materials are commonly used in place of cement-asbestos pipe.

Wooden tanks and gun barrels have an inherent corrosion resistance. The main disadvantage of wooden structures is their high maintenance cost which results from trying to maintain a leak proof structure.

Cathodic protection using sacrificial anodes or rectified current has proven economical for heater-treaters, salt water tanks, and the interior bottom of oil storage tanks. Usually a current density from 10 to 40 milliamperes per square foot of exposed steel is required for protection in a produced water environment. Vessel coatings are often used in conjunction with cathodic protection to reduce the exposed metal area. Typical installations of this type are shown in Chapter 5.

Economics of Corrosion Control

As in any corrosion problem, accurate cost records are needed before a major control program can be justified. This can be a slow and laborious task because of the many variables involved. Records of equipment failures before and after protection are the only true measure of the worth of a control program. Recent work has verified that the savings due to a corrosion-control program are very substantial.

Because of the complexity of the problem, it is sometimes more economical to treat every system, especially wells which handle fluids containing H_2S, than to determine the actual severity of attack in any given field. Key well surveys, whereby detailed equipment performance records are kept on a few selected wells, both treated and untreated, will soon show the value of a corrosion-control program.

Fig. 69 shows an example of such a record and the value of corrosion-preventive treatment is readily apparent.

CHAPTER 4

OXYGEN CORROSION

The most common form of corrosion, the rusting of steel, is an example of oxygen corrosion. The rate of oxygen corrosion may vary depending upon various factors, such as temperature, erosion of the metal surfaces, corrosion films, and availability and type of electrolyte. One of the most important factors is the presence of water serving as an electrolyte. In general, atmospheric corrosion increases with an increase in humidity, i.e., the electrolyte is more available or acts more freely. Oxygen corrosion is usually more severe in salt water than in fresh water (see Chapter 5, Electrochemical Corrosion).

Reducing the supply of oxygen or preventing it from coming in contact with the steel is helpful in reducing oxygen corrosion. One way this can be accomplished is by painting the steel. The rate of oxygen corrosion varies widely with geographic location. As an example, the external surface of equipment used in the Gulf Coast corrodes rapidly, whereas corrosion of the same equipment in the Mid-Continent area will be negligible. The loss due to corrosion depends upon the value of the equipment involved. Corrosion may be undesirable for reasons other than cost, i.e., the safety of operating personnel and the appearance of equipment.

DESCRIPTION OF DAMAGE

Chemistry of Oxygen Corrosion

Although some details of the chemistry of oxygen corrosion are not fully understood, the chemical reaction can be explained as follows:

$$2\,Fe + 3/2\,O_2 + H_2O \longrightarrow 2\,FeO(OH) \longrightarrow Fe_2O_3 + H_2O$$

| Iron | Oxygen | Water | Ferrous Oxide | Ferric Oxide | Water |
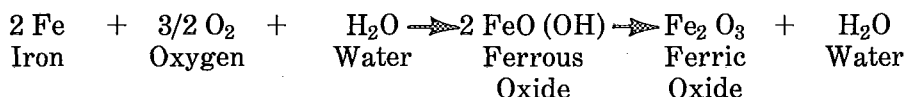
This equation shows that iron combines with oxygen and water to form rust. This type of corrosion can be identified by the $FeO(OH)$ (yellow) and Fe_2O_3 (orange) corrosion products which are seen on steel. The rate of this corrosion reaction depends upon the nature of the corrosion product — whether it is tight and protective or loose and porous. Contact of the metal surface by acid gases, such as carbon dioxide and hydrogen sulfide from natural gas, and by salts from brine, usually increase the rate of corrosion.

Oil Wells

The preceding discussion has pointed out the necessity for air or oxygen to be present before oxygen corrosion can occur. For this reason, oxygen corrosion would not be expected to be prevalent in subsurface oil-well equipment.

Water commonly produced with oil, even when fresh, seldom contains dissolved oxygen. Although most hydrocarbons do not react with oxygen at reservoir temperatures, crude oil contains a number of other organic compounds which react readily with oxygen. Presumably any oxygen originally present in the reservoir would have been consumed by these organic compounds.

Sometimes, however, oxygen corrosion is found in downhole well equipment. When this condition does occur, it is usually caused by careless operating techniques or faulty equipment. A common cause of oxygen entry into pumping wells is an open annulus.

In some fields it is common to take gas from the casing under vacuum. This practice will permit oxygen to enter the annulus when wells are pulled. Air lifting of production introduces oxygen into the well. Air may enter the well with the gas lifting operation if the gas compressor suction drops below atmospheric pressure.

The presence of carbon dioxide and/or hydrogen sulfide increases the rate of oxygen corrosion. Also, as previously stated, oxygen drawn into the well equipment can increase the corrosion rate.

Drill Pipe

Oxygen and fluctuating stresses (fatigue) are considered the principal cause of failure in drill pipe. Pits caused by oxygen corrosion and service scars, such as slip marks and mechanical scratches, concentrate and increase local stresses in drill pipe thus causing cracks to start under the fluctuating or reversing loads. During the drilling operation, the presence of oxygen in the mud aggravates the fatigue action, and this process is

Fig. 72 (right) — Fatigue Cracks at Base of Pits in Drill Pipe
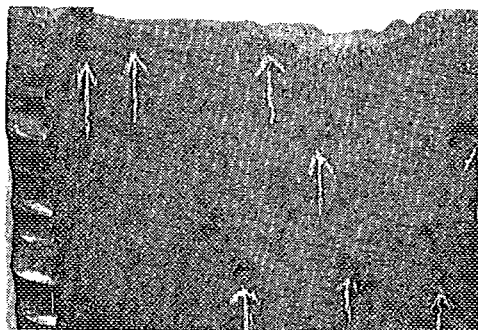
Fig. 73 (below) — Cross Section of Fatigue Cracks at Base of Pit in Drill Pipe

known as corrosion fatigue. As the corrosion pit deepens, corrosion-fatigue cracking proceeds at an accelerated rate. Each of these actions promotes the other, and a vicious cycle is created. Examples of this type of corrosion are shown in Fig. 72 and 73. The failure occurs when a crack or pit progresses all the way through the pipe wall and fluid is forced out. Fluid cutting rapidly enlarges even a tiny perforation until a sizable hole is formed. The pipe, thus weakened, may easily be twisted off.

Exterior corrosion of drill pipe does not localize and form pits, because of continual rubbing on the sides of the hole. Internal corrosion pits are more prevalent and, for this reason, fatigue failures usually start on the inside of the pipe.

Surface Equipment

Oxygen corrosion is generally an exterior problem in primary production equipment. In areas of high relative humidity, serious pitting and overall corrosion can occur as shown on the pumping unit in Fig. 74. The presence of accumulated solids, such as salt, can act as a sponge, absorbing water from the air, thus increasing the rate of corrosion by keeping the surface moist.
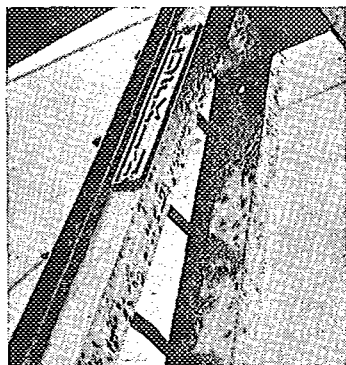
Fig. 74 (left) — Severe Pitting of Pumping Unit Exposed in Area of High Humidity
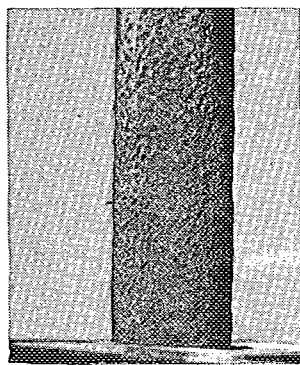
Fig. 77 (right) — Severe Pitting of a Gas Line Exposed to Spray from a Cooling Tower
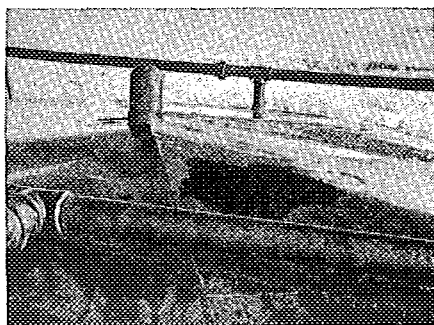
Fig. 75   Fig. 76

Oxygen Corrosion of Stock-tank Deck

The underside of stock-tank decks often exhibits serious oxygen corrosion (Fig. 75 and 76). Breathing of the tank brings air in contact with condensed moisture on the steel surface. The presence of hydrogen sulfide and carbon dioxide increases the rate of attack, as discussed previously in Chapter 3.

Surface piping may show the same general attack as other equipment. Corrosion of pipe exposed to water spray, such as piping in cooling towers, may become extremely severe (Fig. 77).

Water-flood Injection Equipment

Oxygen in oilfield brine or flood water is a major cause of corrosion in this type of equipment. The limited supply of oxygen may cause the formation of distinct lumps called tubercles (Fig. 78). The corrosion product is a soft jelly like material, and deep sharp-bottom pits may occur under this
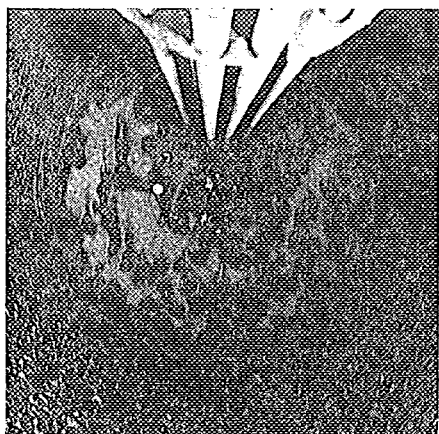
(a) In boiler
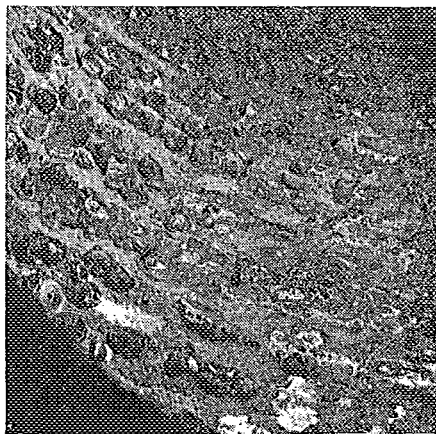
(b) In flowline

Fig. 78 — Tubercules of Oxygen Corrosion Product Caused by Iron Bacteria

deposition. Rapid perforation of the metal, obstruction of flow, and formation plugging by the corrosion products can be expected. The volume of corrosion products compared with the amount of oxygen can be surprisingly large and may cause more damage to the formation than the oxygen would indicate. Small amounts of corrosion products can cause plugging of equipment and also plugging of the formation at injection wells. Oxygen can cause injection well plugging in another way. If the injected water contains dissolved iron or manganese compounds these may oxidize to form insoluble products.

Offshore Operations

Corrosion as it occurs on offshore structures may be divided into three zones of attack. These zones overlap somewhat, and some differences in corrosion rate may be expected within the same zone as designated in Fig. 79. The three zones are:

1. The submerged or underwater zone, where the metal is always covered by water.

2. The splash zone, above the water line, where the wave action usually keeps the metal wet.

3. The spray zone, where the metal appears to be dry most of the time.

In the *submerged* or *underwater* zone, the corrosion tends to be rather uniform. Shallow, general pitting (Fig. 80) is common, and the average corrosion rate is usually 4 to 5 mils per year. (This information was obtained from studies of piling at an Atlantic Coast beach, which differ from structures in other areas.) Where surf breaks against a structure, erosion occurs at the sand line because of the abrasive action of wave-
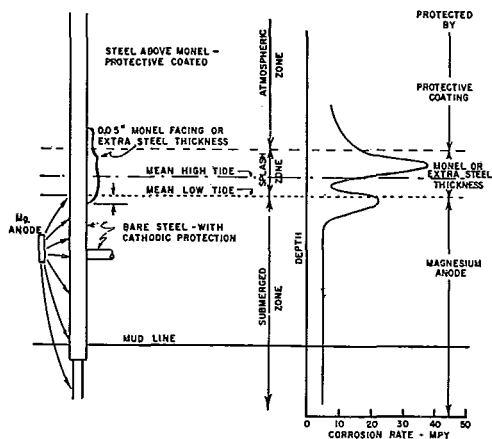
Fig. 79 — Corrosion Rates and Typical Protective Measures of Steel Structures in Various Corrosive Zones
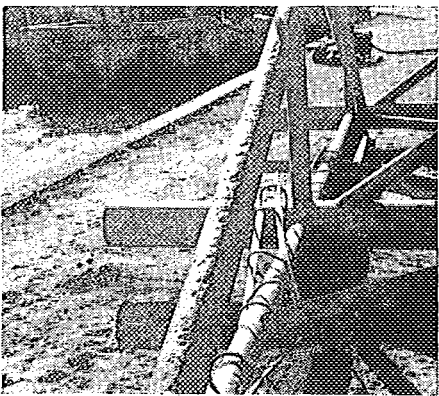
Fig. 80 — Shallow Pitting — Submerged Area — Offshore

Corroded well jacket after two years submersion in Gulf without cathodic protection.

driven sand. This is primarily a problem of erosion; however, corrosion is probably a contributing factor. At some California locations, metal losses at the sand line have been greater than 100 mils per year.

Damage to offshore structures is most severe in the *splash* zone. Here the washing action of well-aerated warm salt water removes corrosion products before a protective coating can be formed, resulting in deep pits. The vertical extent of the *splash* zone depends on the tidal range and the normal height of waves. A greater metal area will be exposed in this zone in the Pacific Coast area than in the Gulf Coast where the waves are not so high.

The design of the structure and method used to join the members can reduce corrosion damage in this zone. Because this zone is the most difficult to protect, it is desirable to limit the number of cross members to a minimum. Experience has proven that welded connections are superior to riveted connections. However, top quality welding is essential. Poor welding may leave crevices that will collect water. Brittle welds may crack and cause immediate failure. Tubular members are easier to protect from corrosion than other types of structural steel.

The *spray* zone usually appears dry, but always has a film of salt on its surface. Night is the time of major corrosion activity in the spray zone. As the structure cools at night and the humidity increases, this salt absorbs water from the air and soon a salty film of moisture covers the surface. The sun dries the film of moisture and reduces the rate of corrosion. The corrosion products tend to flake off in sheets and this irregular spalling of rust promotes pitting. In general, pitting is deeper on the shaded underside of a structure than on the sun-dried upper surfaces.

METHODS OF EVALUATING THE PROBLEM

Thickness Measurement

Thickness measurements offer a direct means of determining the effect of the corrosion. The thickness should be measured at several locations and these locations marked for future reference. Surface scale should be removed before making measurements. The change in thickness divided by the period of time between measurement determines the rate of corrosion. Direct measurement of corrosion pits can also be made.

Corrosion coupons may be helpful in determining the corrosion rate in any given part of the system. Since coupons seldom have the same metal composition as the structure, the corrosion rate is relative. If possible, the coupon should be made a part of the structure to minimize temperature effects and insure uniform exposure to the fluids or environment being tested. As an example, water condenses on the underside of the tank deck, but will not condense on a coupon hung in the vapor space. Therefore, the coupon must be attached to the tank deck as a patch plate to accurately

measure the corrosion rate. Details such as these must be carefully considered when making a coupon survey.

Equipment Failures

Accurate records of equipment failures can be very useful when evaluating a corrosion problem. In some cases, equipment failure records are the only practical way to determine the extent of damage or the effectiveness of remedial measures. Every effort should be made to predict a corrosive condition before failures occur. However, all the information possible should be obtained from failures.

CONTROL MEASURES

Design and Operating Techniques

The basic design of oilfield equipment is usually determined by its use. Attention to minor details may be helpful in reducing corrosion.

Subsurface equipment in oil wells is subject to oxygen corrosion only if oxygen from the air is introduced into the well. As simple a detail as closing the casinghead valve can help in excluding oxygen from the well. In gas lift installations, designing the system to keep all gas lines above atmospheric pressure will, in general, keep oxygen out of the gas. Separator pressures slightly higher than normal will be required and this will necessitate attention to weathering losses caused by these higher pressures.

Drill pipe corrosion fatigue can best be eliminated by decreasing the stress. Pitting of drill pipe can be minimized by flushing the pipe with fresh water each time it is brought from the hole and particularly when it is laid down. The use of drilling fluids with low oxygen content and high pH value is an excellent means of controlling drill pipe corrosion.

Surface equipment should be located to minimize oxygen corrosion. It is good practice to route flow lines around old mud pits and salty or marshy soil. Tank batteries should be placed on high ground or a specially prepared grade for proper drainage.

Injection equipment failures caused by oxygen corrosion can be reduced or eliminated by excluding oxygen. If a fresh water source must be used, consideration should be given to deep wells in which the water is usually free of oxygen.

Corrosion of offshore equipment can be reduced by design and construction. Drains should be arranged to prevent pockets of water from standing on the structures. Welded rather than riveted connections minimize the number of crevices where deep pitting is likely to occur. Tubular sections are preferred. However, when channel sections are used for reinforcement, they should face (or open) down rather than up, to prevent water accumulation. Intersecting members, such as braces, and all other welded connections should be avoided in the splash zone. Fig. 81 shows

examples of design which will minimize corrosion attack. Sharp, acute angles between steel sections should be avoided. This not only gives better load carrying capacity, but also allows better drainage and facilitates surface preparation for painting. Where the design allows condensation to drain off metal surfaces, wear plates should be provided for drain streams and drips. (This is similar to a strike plate in a storage tank.) Extra thickness of steel is frequently used to control corrosion in the splash zone.

Treatment with Corrosion Inhibitors

Inhibitors used to control oxygen corrosion include sodium chromate or dichromate, sodium nitrite, polyphosphates, silicates, soluble oils, and a number of organic compounds. Batch treatment or continuous injection of inhibitor may be used, depending upon the system to be protected. Care should be exercised to insure that the inhibitor reaches all parts of the system. All the inhibitors mentioned are used for treating water used in surface equipment such as heaters, engine radiators, and cooling towers. Even though several inhibitors are available, there is still a need for an improved inhibitor for use in oilfield waters.

Corrosion in oil wells, caused by oxygen, cannot easily be effectively treated with inhibitors; therefore oxygen should be excluded if possible. The types of inhibitors used in drilling muds to prevent drill pipe corrosion are undergoing review because of environmental considerations. It is recommended that the most recent revisions by the environmental authorities be reviewed to select an appropriate, environmentally safe inhibitor.

The Use of Resistant Alloys

It is a rather common mistake to speak of one metal or alloy as being more resistant to corrosion than another, without reference to the entire system. An example may clarify this point. In a humid climate, steel-wire window screens may rust through in a few years, while aluminum screen shows little evidence of corrosion. But in brines, an aluminum tank may
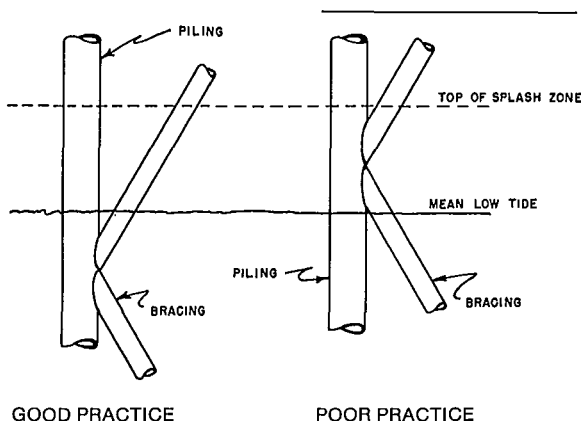
Fig. 81 — Welded Joints and Intersections of Bracing Should Be Either Above or Below the Splash Area

GOOD PRACTICE   POOR PRACTICE

pit and leak in a few months while a steel tank shows little corrosion. The point of this example is that the metal must be chosen with strict consideration for the corrosive environment involved. Experience in similar environments can serve as a guide; however, corrosion resistant alloys must often be selected by the trial-and-error method. The advantages of using alloys for corrosion control are often great enough to justify a test program. On the other hand, resistant metals and alloys sometimes cost no more than common materials which corrode rapidly.

Drill pipe is not made of corrosion-resistant alloys because such alloys are high in cost.

Surface equipment is sometimes made of alloys which are resistant to oxygen corrosion. Brass is used to heat-transfer tubes in some cooling towers. Copper is commonly used in engine radiators. Aluminum alloys are suitable for buildings where sheet steel will rust too rapidly. Galvanized (zinc-coated) steel is widely used and quite effective in resisting moderate oxygen corrosion. The equipment life is dependent upon thickness of the zinc coating. A 2 oz. coating is necessary for maximum corrosion resistance.

Offshore equipment requires large amounts of structural metal and, in general, corrosion resistant alloys are too costly. However, their use in special equipment such as valves, ladders, etc., is standard practice.

For the protection of steel in the splash zone close to the water line, some Gulf Coast operators have used 0.050 in. thick Monel cladding. This is shown in Fig. 82. The cladding has been applied by welding, and more recently by band strapping. Monel is expensive; but because the area involved is relatively small, the use of this alloy can be justified.

Cathodic Protection

Cathodic protection is a method for controlling corrosion under water or in moist soil. This method is discussed in detail in Chapter 5. Here it will suffice to point out that the underwater portion of offshore equipment is usually protected by this method. Cathodic protection is highly successful and economical, but requires careful attention to design and maintenance.

Selection, Application, and Inspection of Protective Coatings

The purpose of this discussion is to outline the main considerations in the application of protective coatings. The reader is urged to refer to the Structural Steel Painting Council's *Steel Structures Painting Manual* for more detailed information on painting practices.

Protective coatings are classified as metallic and nonmetallic. The metallic coatings are either chemically deposited metal oxides, hot-dip zinc, or electroplated chromium, cadmium, zinc, or other metals. Several
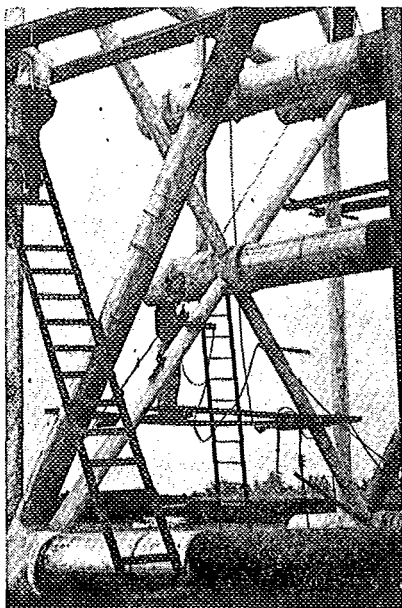
Fig. 82 — Monel (Light Area) in Splash Zone

metals and some plastics can be flame sprayed. Data now available indicate these flame sprayed coatings are porous and may not afford adequate corrosion prevention. These methods of application are not further considered in this discussion, since they are not easily adaptable to field use.

Another group of materials used as protective coatings are slushing compounds. These compounds are used to provide temporary protection to materials in transit or storage and generally are a mixture of oils and wetting agents. They may or may not contain a resinous film building agent. Inasmuch as slushing compounds are used only as temporary protective coatings, they will not be discussed further. This does not, however, imply that the materials are unsatisfactory for their designed use.

The most common type of nonmetallic coating used for corrosion control in oil production is an organic coating. Organic coatings include: asphalt enamel, coaltar enamel, epoxies, phenolics, urethanes, polyesters, chlorinated rubbers, and polyvinylchlorides.

There are certain basic factors which must receive careful attention if satisfactory protective life is to be obtained from a coating application. These are:

1. Conditions of exposure.

   a. Nature of base metal to be protected.

   b. Environment.

2. Surface preparation.

3. Selection of coating materials — primers and top coats.

4. Application of coatings.

5. Inspection.

6. Maintenance of the coating system.

A detailed discussion of these factors follows.

1. Conditions of Exposure

a. *Base Metals.* Proper identification of the metal to which the paint is to be applied is important. Since most of the metal used in oil production is steel, this discussion will be limited to steel surfaces. One exception to this is galvanized steel, which requires special priming techniques.

b. *Exposure Environments.* Most structures for which painting is applicable will be exposed to one or more of the following conditions:

Atmospheric — The atmosphere may vary from neutral in rural areas to highly saline near coastal areas, or with varying chemical contaminants, if located near chemical-process operations..

Water Immersion — The water may be salty, neutral, fresh, acidic, hydrogen sulfide water, or polluted water of various kinds. Marine organisms may become an important factor in marine immersion.

Alternate Atmosphere-Water Exposure — This type of exposure may be any combination of the foregoing; and, in many cases, may prove more severe than either.

2. Surface Preparation

Proper surface preparation is the major factor in determining the maximum service life of a coating outside the quality of the coating itself. Applying a good coating to a dirty, greasy, or rusted surface is an expensive "economy". Premature paint failures mean more than the loss of paint, since labor and the other costs of application average 250 to 800 percent of material costs.

The degrees of surface preparation practical from an economical viewpoint will depend upon: *1*, the condition of surface; *2*, the wetting characteristics of the material to be applied; *3*, the type of paint to be applied; and *4*, the severity of the exposure.

The methods of surface preparation are divided into two general classifications — mechanical and chemical. The mechanical methods include wire brushing, flame cleaning, and the three degrees of sand blasting. The chemical methods include acid pickling, emulsion cleaning, akaline cleaning, and solvent cleaning. Where their use is permissible, mechanical methods of surface preparation are preferred.

A. *Sandblasting* is generally recognized as the preferred method of surface preparation. In all cases the anchor pattern of the blast should not exceed one third of the total thickness of the paint film. As an example, if a 6-mil paint film is to be specified, the maximum blast anchor pattern should not exceed 2 mils.

Sandblasting is generally classified into three categories.

a. *White surface blasting,* which completely removes all corrosion particles, all mill scale, and the gray oxide binder between the steel and the scale.

b. *Commercial blasting,* which removes all corrosion products and all mill scale, but does not remove the gray oxide binder.

c. *Sand brush-off or sweep blasting,* which removes only corrosion products and the loose mill scale. Tight scale is not removed, but does receive an anchor pattern.

Sandblasting may be accomplished by an open dry system, a closed dry system, an open wet system, or a closed wet system. In the closed systems, the abrasive is re-used and, generally, is more applicable to shop installations.

B. *Power wire brushing* has, in some cases, been accepted as a satisfactory practice. If conscientiously carried out, loose and seemingly tight scale can be removed. It is not practical to remove tight mill scale by this method. It is imperative that power brushing be followed by solvent washing prior to the application of paint.

C. *Hand wire brushing* is the least desirable method of surface preparation and, according to some authorities, is inferior to no preparation at all. This method will generally remove only loose corrosion products and loose patches of old paint. After wire brushing, the surface should be brushed or swept and then blown off with compressed air to remove loose dust and foreign particles.

D. *Acid pickling* is generally used by fabricators to remove oxide films which have formed by rusting or heating. This method is mainly used as a shop process for surface preparation.

E. *Alkaline, emulsion, and solvent cleaners* are used only where it is desired to remove grease, oil, or surface soil and are generally not used as prime methods for surface preparation.

3. Selection of Coating Materials

The effectiveness of a coating system is dependent upon two main functions: its ability to seal the metal from the corrosive environment, and its ability to inhibit corrosion when the corrosive agent does permeate the film. To form an effective seal, a coating film must be: *1,* continuous, free of holes or breaks; *2,* impermeable to water vapor and other gases; *3,* adherent to the base metal and coherent; *4,* chemically inert against hydrolysis, oxidation, sunlight, and temperature deterioration. The selection of a specific coating will depend upon the surface preparation involved. This surface preparation will affect the degree to which a coating material can wet the metal and form a smooth, continuous coat. Also, the adhesion of a coating will be influenced by surface preparation and must be considered. Most coating systems involve primers and top coats. The primer is selected to bond the top coat to the metal and inhibit the corrosive action of any agent which may permeate the film or reach the primer as a result of physical breaks in the top coat. The main purpose of

the top coat is to form the actual barrier or seal against the corrosive elements. On new paint application it is recommended that a minimum of two coats of alternating colors be used. The practice of alternating colors of each coat serves two purposes: *1.* It aids in obtaining complete coverage and provides a guide for repainting. *2.* It is generally good practice to recoat with one top coat when the next color coat becomes visible. The selection of any coating system will depend upon the environment to which it is exposed, and for that reason only generalizations can be given in this manual.

4. Application of Coatings

The expense of excellent surface preparation and the cost of the best coating materials can be lost if precautions are not taken to insure their proper application.

Paint must be applied to a dry surface. Coating should not be applied when the relative humidity is above 85 percent or when the atmospheric temperature is below 40 F. The optimum temperature for application is 60 to 80 F. At lower temperatures there is danger of moisture condensing on the surface.

Selection of proper spray equipment will vary with the material to be applied and the nature of the structure to be coated. The coating manufacturer's recommendation on equipment should be considered.

5. Inspection

Specifications for surface preparation and paint application are prepared for a guide to be used by both the inspector and the contractor. It is the inspector's responsibility to see that they are followed. A properly trained, conscientious inspector can be the difference between a good or poor coating job.

A. *Inspection of Surface Preparation.* During surface preparation it is the inspector's responsibility to see that:

a. The surface is cleaned to the degree specified.

b. The proper anchor pattern is obtained.

c. No damage or contamination of freshly painted areas adjacent to cleaning operations occurs.

d. Compressor traps are blown down to remove moisture and oil.

B. *Inspection of Paint Application.* An inspector of a paint application is responsible for:

a. Checking the surface to see if it has become contaminated since preparation.

b. Determining if the materials on the job are those called for in the specifications.

c. Checking mixing and thinning operations.

d. Daily checks of temperature and relative humidity.

e. Allowing proper drying time for all coats.

f. Determining if sufficient film thickness is being obtained.

g. Checking cleanliness of contractor's equipment.

6. Maintenance Painting

If a properly organized maintenance painting program is put into effect, it will seldom be necessary to do more than clean isolated areas of paint deterioration, spot prime, rebuild the coating system, and apply a new top coat to the entire area. If it becomes necessary to remove the remaining coating from the entire area, then the inspector's duties will be as outlined.

CHAPTER 5

ELECTROCHEMICAL CORROSION

Almost always, corrosion is electrochemical in nature. This simply means that some amount of electric current flows and can be measured when corrosion is occurring. This chapter will outline some simple experiments that demonstrate the electrochemical nature of corrosion.

DESCRIPTION OF DAMAGE

Chemistry of Reaction

There are two basic types of electrochemical corrosion. The first type, which is a sort of reverse plating operation, occurs when direct currents leave an underground pipe system. At one time this was frequently caused by currents from electric railways. The most common cause of this stray-current damage in the oilfields of the present day is improper cathodic protection. The second and by far most common type of electrochemical corrosion is that which occurs naturally when pipe is exposed in moist soil.

In previous chapters, oxygen and acid have been referred to as corrosive agents. In electrochemical corrosion they are still considered the corrosive agents, but we are also considering the electrical effects that can be produced. A simple experiment will demonstrate this. When a piece of zinc is immersed in dilute hydrochloric acid or sulfuric acid, bubbles of hydrogen are given off at the surface of the zinc (Fig. 83). When a piece of copper strip of about equal or greater area is connected to the zinc strip by a wire and both zinc and copper are immersed in the same glass of acid, most of the bubbles now appear on the copper. The zinc is the metal that is corroding; but, through the electrical effects, the point where bubbles are evolved has been changed. This experiment shows that the electrical characteristics of a system are important.

The words used to describe electrochemical corrosion are not very common, so they must be mentioned and explained. In the experiment described, the metal that corrodes — in this instance, zinc — is called the "anode" and the metal that does not corrode is called the "cathode." Hydrogen bubbles, as well as zinc that is dissolved in the acid, are called "corrosion products".

More complicated corrosion cells illustrate a few more terms. Steel pipe in the ground is exposed to moist soil containing some dissolved salts and with varying contents of oxygen. This can be represented by Fig. 84. As an experiment, one strip of steel can be put in a jar of salt water with a second piece of steel surrounded by a funnel made of filter paper or paper immersed in that same jar. The funnel serves to prevent mixing of solutions, but will still allow current flow. After the two strips are firmly con-

nected with a wire, gently blowing air in the salt water in the funnel will cause the strip which has less air to corrode. Salt water in this experiment is called the "electrolyte". The air, which causes the corrosion to go on, is the "corrosive agent"; or, more particularly when applied to electrochemical cells, it is a "depolarizer" for reasons to be mentioned next.

Metals vary in their tendency to dissolve, just as sugar has a greater tendency to dissolve than does the scale which forms in oil well tubing. Metallic iron goes into solution as electrically charged particles or atoms of iron. These electrically charged particles are called "ions". As iron goes into solution, it tends to force hydrogen out. When the tendency is great enough, as with iron in hydrochloric or dilute sulfuric acid, bubbles form.

Fig. 83 (right) — Zinc — Copper Cell

When zinc is coupled to copper in a hydrochloric acid solution, zinc goes into solution and hydrogen plates out at the copper cathode.
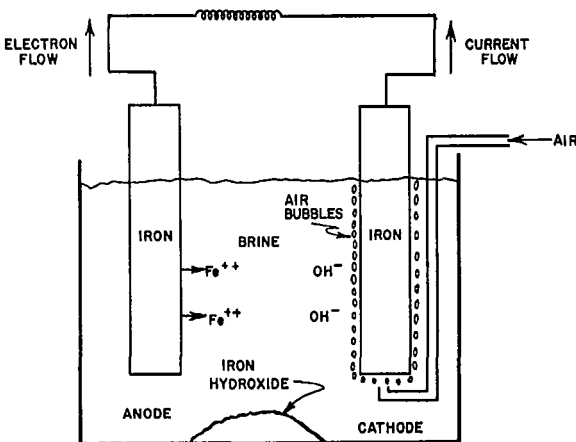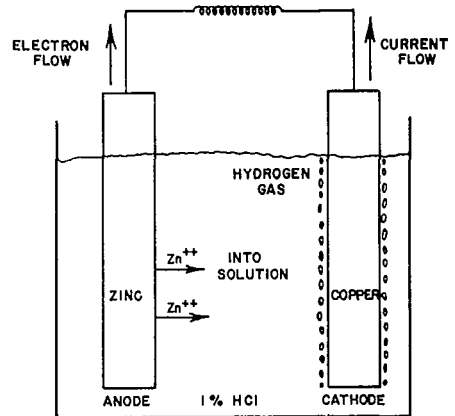

Fig 84 (left) — Iron — Iron Cell

In a brine solution the unaerated electrode becomes anodic and corrodes, while the aerated electrode becomes the unattacked cathode. Ferrous and ferric hydroxide precipitate when the iron ions unite with the excess hydroxide products at the cathode.

Copper has much less tendency to go into solution and to evolve bubbles of hydrogen, so that very strong acids and temperatures near boiling are required. There is still one other way in which hydrogen can be removed. It can be reacted with oxygen, as available from air, to form water. This is also illustrated in Fig. 84. When the buildup of hydrogen is not removed, the cathode is said to be "polarized". Reaction of the hydrogen with oxygen is a "depolarization" reaction.

In this cell of Fig. 84, the electrically charged atoms of iron react to form rust some distance from either cathode or anode. When the distance between cathode and anode is very small or when there is a great deal of the rust or scale, the corrosion product tends to cover both anode and cathode and may slow down the reaction. As a result of the corrosion products covering one surface or the other, they may cause a reversal of the position between anode and cathode; that is to say, what was once the protected area can become the corroding area.

What determines how fast a metal corrodes? The answer to this is closely related to the rate of flow between two tanks. If the two tanks have the same level there is no tendency for flow and there is no flow. If the levels are different, the rate of flow depends upon the difference in level as well as pipe size, how far open the valves are, the length of pipe connecting the two tanks, etc. In corrosion work under very standardized conditions it is possible to use tables that give the level of corrosion tendency very much as it is possible to state the level of tanks in elevation above sea level. Such tables are known as "electromotive series" or "galvanic series" (Tables 1 and 2). These tables do not give the other factors that correspond to the determination of rate of flow, such as the length of line or line sizes, so they do not state how fast a metal actually corrodes. They simply state its tendency. Calculating just how fast a metal will corrode is very complicated.

Bimetallic Corrosion

Fig. 83 was used before to illustrate the fundamental process of corrosion. A very particular type of cell — the bimetallic cell — is also illustrated by Fig. 83. Coupling copper to the zinc with a wire allowed a higher rate of corrosion to occur on the zinc than would normally occur if there were no electrical connection to the copper. This coupling of zinc to the copper did not cause corrosion, although it did increase the corrosion rate on the zinc. The real cause of the corrosion was the acid. The copper was protected at the expense of the zinc. In Fig. 85 acceleration of corrosion of an iron nipple has been caused by a copper-containing bronze seat.

One fairly general rule indicating the acceleration of damage in a bimetallic couple is the "area principle". This rule states that the total corrosion is proportional to the total area exposed to the corrosive electrolyte. If there is a marked tendency of one metal to corrode in preference to

Table 1

Electromotive Force Series

	Standard Electrode Potential, $E°$ (volts) 25 C.
Potassium (K)	-2.922
Calcium (Ca)	-2.87
Sodium (Na)	-2.712
Magnesium (Mg)	-2.34
Beryllium (Be)	-1.70
Aluminum (Al)	-1.67
Manganese (Mn)	-1.05
Zinc (Zn)	-0.762
Chromium (Cr)	-0.71
Gallium (Ga)	-0.52
Iron (Fe)	-0.440
Cadmium (Cd)	-0.402
Indium (In)	-0.340
Thallium (Tl)	-0.336
Cobalt (Co)	-0.277
Nickel (Ni)	-0.250
Tin (Sn)	-0.136
Lead (Pb)	-0.126
Hydrogen (H_2)	0.000
Copper (Cu++)	0.345
Copper (Cu+)	0.522
Mercury Hg+)	0.799
Silver (Ag)	0.800
Palladium (Pd)	0.83
Mercury (Hg++)	0.854
Platinum (Pt)	$1.2*$
Gold (Au+++)	1.42
Gold (Au+)	1.68

*Approximate.

Table 2

Galvanic Series of Metals and Alloys*

Corroded End (anodic, or least corrosion-resistant)

Magnesium and Magnesium Alloys
Zinc
Aluminum 1100 (2S)
Cadmium
Aluminum 2017 (17ST)
Steel or Iron
  Cast Iron
Chromium-iron (active)
Ni-Resist Cast Iron
Type 304 Stainless (active)
  Type 316 Stainless (active)
Lead-tin solders
  Lead
    Tin
Nickel (active)
  Inconel (active)
Brass
  Copper
    Bronzes
      Copper-nickel alloys
        Monel
Silver solder
Nickel (passive)
  Inconel (passive)
Chromium-iron (passive)
  Type 304 stainless (passive)
    Type 316 stainless (passive)
Silver
Graphite
  Gold
    Platinum
Protected End (cathodic, or most corrosion-resistant)

*From International Nickel Company's *Nickel and Nickel Alloys*, Section D.

another — such as iron and copper exposed in aerated salt water — the less-resistant suffers the entire corrosion. It is better to spread the corrosion potential over a large area rather than concentrate it in a small area. The less resistant metal should have greater surface area (see Table 2). Thus steel rivets in Monel or copper sheet corrode very rapidly; Monel rivets in steel plate cause little damage.

The area principle should be used with some caution. As an example, a copper wire might be coupled with a sheet of aluminum in a tank of stagnant aerated water. After a while copper would plate out on most of the surface of the aluminum, and the area of copper would be very much greater than a casual glance would indicate.

Fig. 85 — Accelerated Corrosion

Electrochemical corrosion caused by bimetallic junction. Bronze seat as cathode — steel the anode.

When corrosion-resistant alloy steels were first used in condensate wells, their effect in accelerating corrosion of the casing was studied. It was feared that coupling nickel or chromium steels with N-80 casing would result in severe corrosion of the casing. Practical experience demonstrated that the system was soon polarized; that is to say, corrosion did not proceed. The important point to be learned from this example is that coupling dissimilar steels together in a neutral non-aerated electrolyte will not cause corrosion. Some corrosive agent such as oxygen is required to continue the reaction. The electrolyte has to be corrosive to at least one member of the dissimilar metal couple if there is to be bimetallic corrosion.

The area principle can be applied to pitting of steel pipe. As it comes from the steel mill the pipe is usually covered with mill scale. This mill scale is a fair conductor of electricity and, at the same time, it is also insoluble in water and weak acid. This means that the areas covered with mill scale are protected and act to concentrate the corrosion where there is no mill scale. After a while the mill scale loosens. Consequently, the acceleration of attack is important only in the early life of the pipe. Good examples of bimetallic corrosion caused by mill scale are shown in Fig. 86. The tubing is from a well in which acid got into the annulus during the acidizing process. Mill scale concentrated the corrosion effect on the patches of bare metal immediately adjacent to the mill scale (Fig. 86a).

Fig. 86 — Bimetallic Corrosion Caused by Mill Scale on Steel Tubing
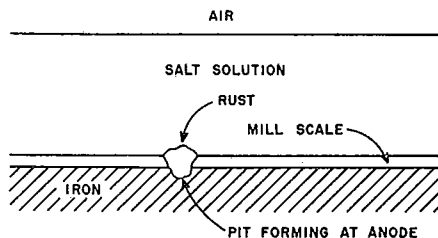
Fig. 86a — Galvanic Corrosion of Iron due to Mill Scale
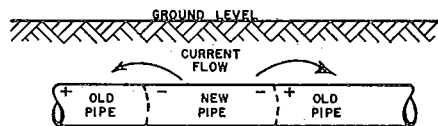
Fig. 87 — Electrochemical Corrosion by New Pipe

New sections of pipe in an old line are sometimes attacked because the old pipe is covered with heavy layers of oxide and rust which are cathodic to the new pipe (Fig. 87).

Speller[1] blames much of the early pitting of steel pipe exposed to water on the presence of mill scale on the surface. Iron sulfide on steel surfaces in various pieces of oil-well equipment causes similar attack.

Concentration Cells

The tendency of a metal to corrode depends not only on the metal itself, but also to what it is exposed. As illustrated in Fig. 84, iron exposed in the aerated solution is uncorroded and thus is a cathode, while the iron in the unaerated solution corrodes. Fig. 88 shows this same effect with a drop of salt solution. The outer ring of the drop where the oxygen content is highest does not corrode, while the metal under the center of the drop corrodes. This type of pitting action is called "concentration cell" corrosion. When oxygen is the agent causing the damage the cell is called "oxygen concentration cell".

Figure 88 also includes another type of cell — the "metal ion concentration cell". The higher concentration of iron under the center of the drop somewhat reduces the tendency to corrode. However, when iron corrodes

[1]Speller: *Corrosion, Causes and Prevention,* 44, McGraw Hill Book Co., Inc., New York, 1951, 3rd Edn.
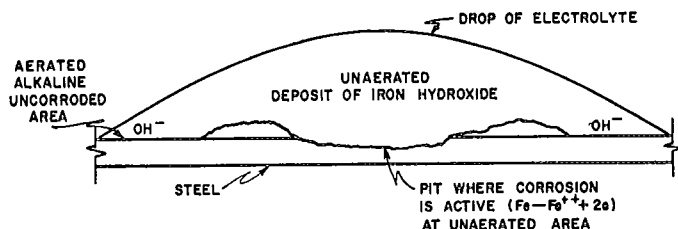
Fig. 88 — Magnified Cross-section of Drop of Electrolyte on Steel

The edges of the drop are high in oxygen; the center low in oxygen.

in aerated solutions, this tendency is not very important. When copper corrodes, the metal ion concentration has considerable effect. Since this metal ion concentration cell opposes the oxygen concentration cell, it is an important reason for the resistance to pitting of copper. Metal ion concentration cells are too weak to be of any significant effect on corrosion of such active metals as aluminum, zinc, and magnesium. Carbon dioxide and hydrogen sulfide cause concentration cell effects on iron, but they have not been studied in detail.

Soil Corrosion of Pipe and Surface Equipment

The characteristics of soil can affect corrosion. In the cells mentioned previously there was also some sort of a salt present, and these salts participated in the current flow. Pure water is a poor conductor of electricity, and corrosion in pure water is considerably different from what would ordinarily be experienced when salts are present. Sandy soils very frequently have no salt present, with the result that very little current flows, and no significant pitting and localizing of attack occurs.

Of course, water must be present to allow appreciable currents to flow through the soil. Steel does not corrode in very dry weather. In the same way, corrosion in very dry soils is negligible. Water and the high concentrations of salt account for the severe corrosion found where lines go under slush pits. Oxygen is still the real corrosive agent; the water and the salt allow it to act and pit the steel.

Limestone has still another effect. It allows a chalky layer (calcareous) to form a somewhat protective coating on the pipe in the cathodic area. This reduces the amount of surface available for reaction and thus decreases corrosion. Organic material, like decaying vegetation, is generally acid. At the same time, there is a deficiency of oxygen which, when combined with the acidity, results in severe pitting of the oxygen concentration cell type. This effect makes it desirable to insulate from each other those sections of pipe exposed to markedly different soil conditions — unless, that is, both sections are under good cathodic protection.
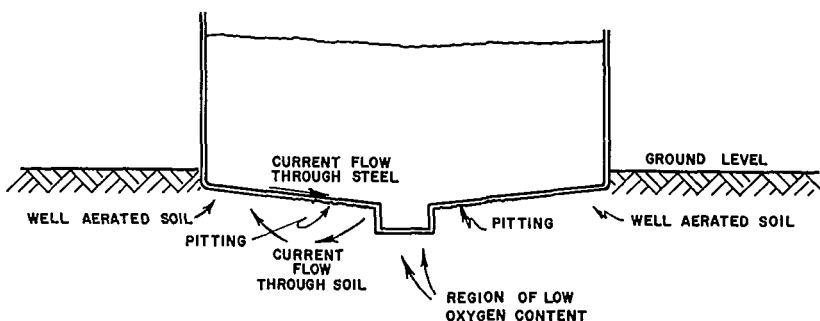
Fig. 88a — Pitting on a Tank Bottom

Not only is pipe affected by electrochemical corrosion, but so is all steel equipment in contact with the soil. Large areas of tank bottom surfaces are exposed to soil which has little access to oxygen. This leads to severe tank bottom corrosion illustrated in Fig. 88a.

Casing Corrosion

Casing is, in one sense, the last of fluid containment. Hence casing corrosion, internal or external, is a serious matter. Internal corrosion has been studied in a previous chapter. The discussion in this chapter will be confined to external corrosion of casing.

External corrosion has been ascribed to an electrochemical type of attack resulting from a current transfer caused by a potential difference between two parts of a well. These potential differences may be between:

1. Casing in contact with one formation and another.

2. Casing in contact with one formation and a mud cake.

3. Surface flow line and casing.

4. Surface pipe and casing.

5. Areas of dissimilar metallurgy.

Fig. 89 shows electrochemical action between two formations, A and B. In the anode area, oxidation takes place as iron ions go into solution in formation A as a product of corrosion. In the cathode area, reduction takes place and hydrogen atoms are formed at the boundary between the pipe and formation B. The flow of current is into the formation at the anode or corroding area and into the pipe at the cathode. As this battery action takes place, the layer of hydrogen developed on the cathode offers a resistance to the flow of current in the cell. The cathode thus has been polarized. This polarizing film can be removed by mechanical action or by the addition of a depolarizing agent which reacts with and removes this hydrogen film. Such an agent must be present in order for this corrosion reaction to proceed at a rate sufficient to cause a severe corrosion problem.

Fig. 89 — Section between Two Formations Resulting In Electrochemical Corrosion of Casing.
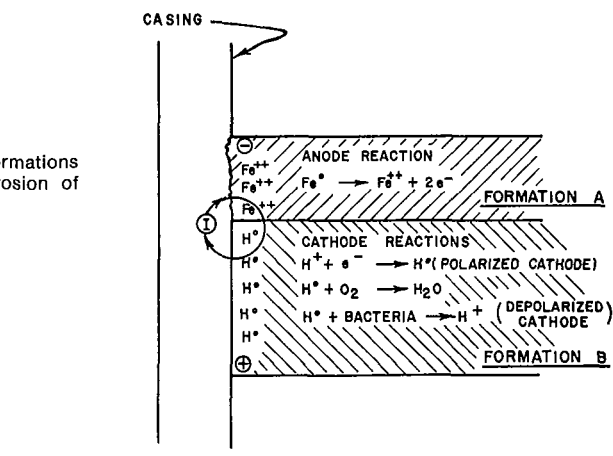
Two common depolarizing agent are:

1. Oxygen which reacts with hydrogen.

2. Certain bacteria which use atomic hydrogen as part of their life process.

When the surface line pipe or a portion of the casing or surface pipe down to a few hundred feet in the well is the cathode, oxygen is an obvious depolarizing agent.

When the cathode is at greater depths, it seems likely that the sulfate-reducing bacteria are a major factor in casing corrosion. They may originally be in the wells or be introduced through the mud system. The role of suflate-reducing bacteria as a factor in causing corrosion is still controversial. But to doubt their role as cathodic depolarizers is to ignore the results of significant research undertaken by competent corrosion engineers.

METHODS OF EVALUATING THE PROBLEM

Recognizing Electrochemical Corrosion

Although there are no foolproof ways to determine whether or not it was electrochemical corrosion that caused damage to a piece of equipment, there are common features to this type of attack. On pipe the best indication is isolated areas of severe pitting. On other equipment, such as a valve, severe corrosion at the junction of dissimilar metals may indicate bimetallic attack. Corrosion-erosion can sometimes be confused with bimetallic corrosion, although there are generally indications of velocity effect.

Observation of the ground features can supply valuable information. Areas with heavy vegetation, poorly drained soil, or those contaminated by oil well brines are possible trouble spots. These should be examined first if damage is suspected.

Current and Potential Measurements

Even though it is not always possible to actually see the equipment in question, there are methods that can be used to measure either the current or the potential involved and from this data estimate likely corrosion damage. One way to measure the current flowing in a line is to break the line and bridge the gap with an ammeter. Line currents may also be measured indirectly by using a voltmeter if the resistance of the pipe is known. In this method the IR drop is obtained by connecting the voltmeter leads to each end of a known distance of pipe. The current can then be determined by applying Ohm's law — current equals voltage divided by resistance. Another method is to balance out the current in the line and then measure the balancing current. Currents as high as 2 amp are frequently encountered.

The resistivity of the soil is very important in the corrosion of underground installations. Soils with a resistivity of less than 1,000 ohm-centimeters are capable of serious pitting, whereas those soils with a resistivity greater than 10,000 ohm-centimeters are rarely corrosive. Soils of lower resistivity can be made virtually non-corrosive with cathodic protection. By pipe-to-soil potential determinations and by surface potential readings, corrosion engineers can determine where current is leaving the pipe and in this manner locate the "hot spots" (places where corrosion is most apt to occur). Techniques for measuring current, potential, and soil resistance are discussed in more detail in the appendix.

Oil well casing presents a different problem. The actual extent of external corrosion may never be determined since casing is rarely pulled. A logging method has been developed for measuring corrosion current. In this method, an electrical probe is run with tubing and rods out of the hole and with the flow line disconnected. The electrical potential difference is then measured at 25 ft intervals. The current may be calculated using Ohm's law. The plot of potential difference vs. depth is termed a *casing potential profile*. This profile, Fig. 90, shows that, where the curve slopes upward and to the right, current enters the pipe and the section does not corrode (areas A and D). When the curve slopes upward to the left, current is leaving the pipe and corrosion may occur (area C). If there is no current entering or leaving the pipe, such as in area B, corrosion is not apparent. The most important feature of the profile is that the slope shows the rate at which current enters or leaves the pipe. When anodes and cathodes are closer together than the electrode spacing of the tool, corrosion cannot be evaluated. Typical field data from a Kansas well are shown in Fig. 91. The anode area from 900 to 1,300 ft corresponds to the Dakota formation opposite which many external casing areas such as shown in Fig. 92 are found.

Good correlation has been obtained using this method. It has been determined that 1 to 5 amp are usually sufficient to remove anodic areas

Fig. 90 (right) — Casing Potential Profile
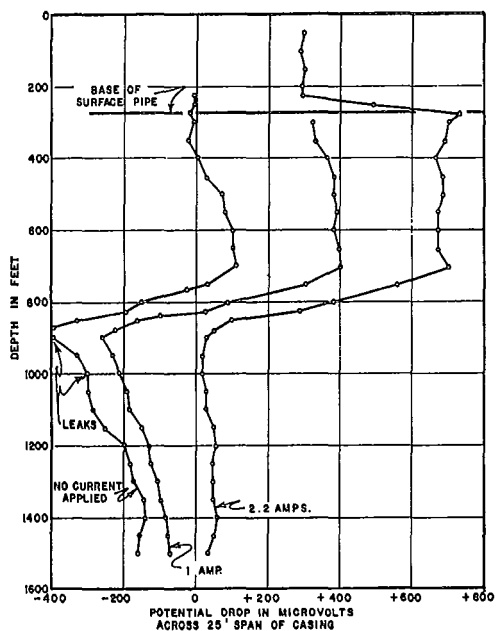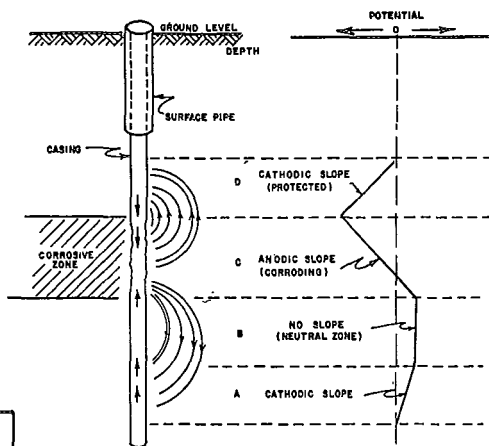
Fig. 91 (left) — Potential Profile of Kansas Well

Corrosion occurs in zone 900-1,300 ft, opposite Dakota Zone.
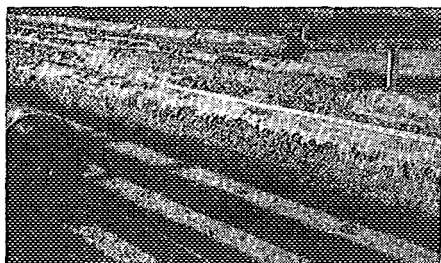
(a) Severe external corrosion occurred in two years in area defined as anode by casing potential profile. Severe casing corrosion occurred on area of casing caked with mud.
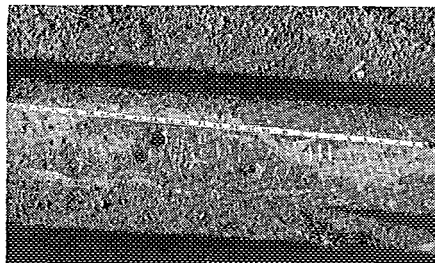
(b) Severe external corrosion occurred in two years in area defined as anode by casing potential profile. Severe pitting.

Fig. 92 — External Casing Corrosion

up to 6,000 ft in depth. In a test on one well it was found that 7.5 amp impressed current actually caused potential changes to a depth of 8,700 ft.

Failure Records

Records of failure of equipment are a positive method of determining where corrosion is a problem. If a large number of leaks have occurred in a given locality, it is apparent that this area should be investigated and perhaps protection should be applied. By maintaining accurate performance and corrosion records, protection of equipment and the prevention of leaks can be accomplished with a minimum of effort. Whenever an inspection, installation, or workover is performed, special attention should be given to the condition of the equipment. Has corrosion been active? If so, where is the damage and why? How severe is the attack? Answers to questions like these are valuable aids in mitigating corrosion under any circumstances.

CONTROL MEASURES

This chapter is primarily concerned with electrochemical corrosion. Hence, control measures are concerned with breaking, reducing, or reversing the direction of current flow. The former can be accomplished in many cases by taking adequate precautions during the design stage of installations. The reversal of current flow is accomplished by cathodic protection.

Design

To minimize well-casing corrosion, it is generally desirable to insulate electrically the surface lines from the well equipment, Fig. 93 and 94. The surface lines are generally cathodic, while the casing in favorable strata is the anode. It sounds simple to insulate the casing from the surface equipment, but adequate insulating is usually difficult. A simple test for determining the effectiveness of an insulated joint is shown in Fig. 94a.

Meter bypasses, bolts at flanges, grounded neutrals of the electrical system, remote indicating devices, small inhibitor lines, etc., may also completely nullify efforts to insulate the casing. When electrical grounding is necessary as protection against short circuits, this can be attained by connecting the ground wire to one or several magnesium anodes. If there is a ground wire, such as the grounded center of a 4-wire 3-phase star connection or a 3-wire 110-220 volt line, there is no adequate way to ground electrically and still keep the casing insulated from surface equipment.

If it is known that a particular shallow zone is always corrosive in a given area, it may be economical to run surface pipe a little deeper to protect against the offending zone. This technique is frequently used.
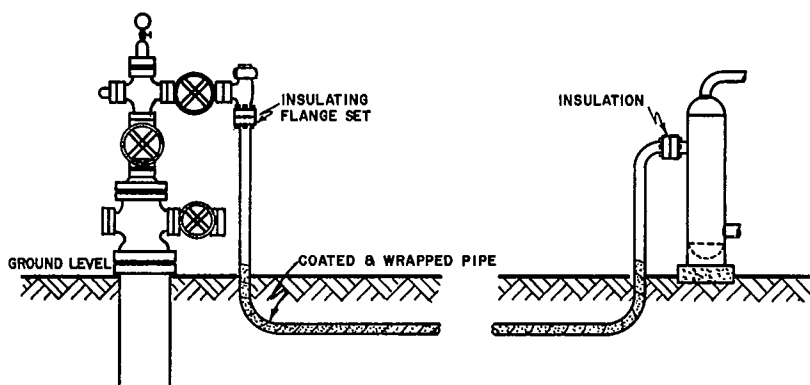
Fig. 93 (above) — Insulating Flange to Stop Current Flow between Well Casing and Surface Equipment
It is important that *all* surface equipment be so insulated.
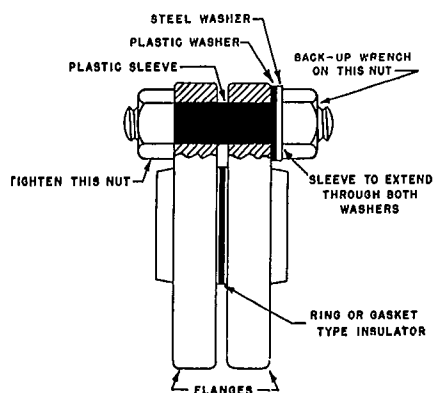
Fig. 94 (left) — Assembly Make-up of an Insulated Flange

Fig. 94a (right) — Testing Insulated Joint for Short Circuit
(a) Lamp will be dim if no short circuit and bright if short circuit.
(b) Needle of compass will move if current passes through short-circuited joint.
(c) Under one condition, when a large potential difference exists across the joint, the lamp might indicate bright although joint is insulated.
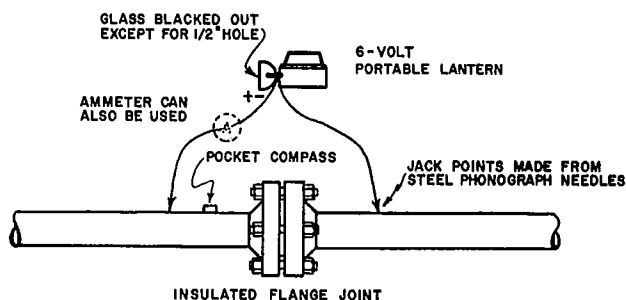
The corrosion reaction caused by underground water zones can sometimes be stopped or minimized by cementing off the offending zone. If it is suspected that water is moving from one zone to another through a path along the casing, cementing is probably the best solution.

In some areas, where sulfate-reducing bacteria are thought to be a major factor in casing corrosion, a bactericide can be incorporated into the mud system during completion of the well to kill the bacteria. This has been tried in several wells. The long term effectiveness of this program is not yet known.

Impressed direct current (stray current), like the current from a d-c welding generator, adds energy to the system and causes unpredictable corrosion. One ampere flowing for one year at 100 percent current efficiency removes 20 lb of iron. Since pitting generally results from stray currents, the damage is severe. The best way to counter this is to break the connection between the offending equipment and the pipe or casing suffering the corrosion.

Occasionally cathodic-protection systems using rectifiers may interfere with unconnected pipe to cause corrosion, Fig. 95. The currents flowing through the earth jump on the pipe and then jump off at another point. This is most likely to occur near the rectifier ground bed. Corrosion caused in this way can be mitigated by bonding the corroded line into the cathodic-protection system. This should be done by qualified personnel, since the effectiveness of the protection can be lost by improper bonding.

On the underside of tanks, pitting can be quite concentrated at un-oxygenated areas because of oxygen concentration cells (Fig. 92a). If cathodic protection of the steel tank bottom is not contemplated, the tank should be placed on a well-drained location and on thick layers of clean rock and sand. Thin layers of rock and sand are ineffective in practically all instances since the bottom of the tank will not be elevated above the

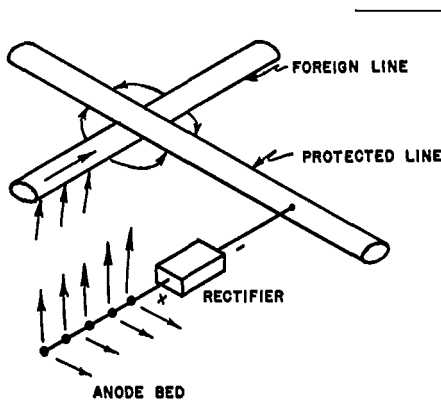Fig. 95 — Interference

Some of the current flowing from the anode bed to the protected line collects on the foreign line, flows along it toward the crossing (from both sides), and then discharges through the soil to the protected line. Damage is inflicted on the foreign line in the neighborhood of the crossing.
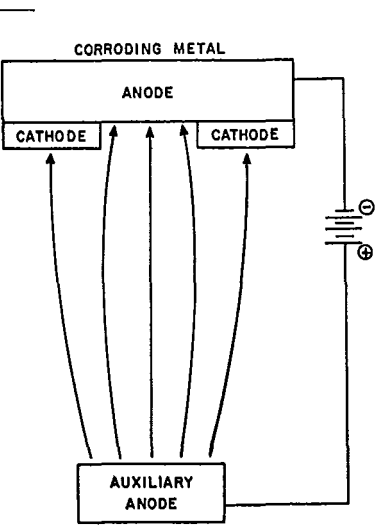

Fig. 96 — Applying Protective Current to a Typical Electrochemical Corrosion Cell

height of capillary water rise, and a continuous film of water may always be present. This water furnishes the conductivity necessary for corrosion. As an added disadvantage, porous foundations allow a greater amount of oxygen to be present to act as a depolarizer and increase the total metal removal.

The inside surfaces of tanks are also subject to electrochemical corrosion. Generally this is manifested by isolated areas of pitting. Cement linings, plastic coatings, cone bottoms, and inhibitors are the most commonly used methods of mitigating corrosion in storage tanks. Frequently, one or more of these is used in conjunction with cathodic protection of storage-tank bottoms.

Cathodic Protection

For many years, cathodic protection has been used widely for control of electrochemical corrosion in the oilfield. A simplified diagram, Fig. 96, illustrates a typical installation. Cathodic protection is simply the installation of an anode which results in a direct electrical current on the metal being protected, causing it to be a cathode. The source of this current may be magnesium, high-purity zinc, aluminum alloys, or an external power source using a rectifier and a ground bed. The choice of current source depends upon each individual set of conditions. In either case the anode is electrically bonded to the metal being protected. The current path is completed through an electrolyte (in this illustration, the wet earth).

It should be remembered in all this discussion that cathodic protection is of value only to the surface of the steel exposed to the same electrolyte as the anode.

Determining the minimum current requirements for adequate protection of a system is very important. In soil, the effectiveness of such a system depends upon the resistance of an electrolyte and condition and size of the structure. The actual current needed is calculated in terms of current density, i.e., amperes per square foot. For normal conditions on buried bare pipe, current densities of about 1.0 milliamperes per square foot are required for protection, but this value may vary greatly depending on local conditions. Coated pipe requires considerably less current.

Another criterion used is that of the potential of the structure to electrolyte. In general, a potential of —0.85 volts, as measured with a copper — copper sulfate half cell, is considered safe. Corrosion rate increases as this value becomes more anodic (or less negative).

In some cases of high soil resistance this criterion is not useful. In such cases, it is found that changing the pipe-to-soil potential by 0.2 to 0.3 volts is generally sufficient to stop corrosion.

In many cases, cathodic protection can be attained only through the initial use of high current densities. This practice is called pre-polarization

Fig. 97 — Hard, Thick, Porous Calcareous
Scale Typical of that on Pipe Exposed to
Cathodic Protection
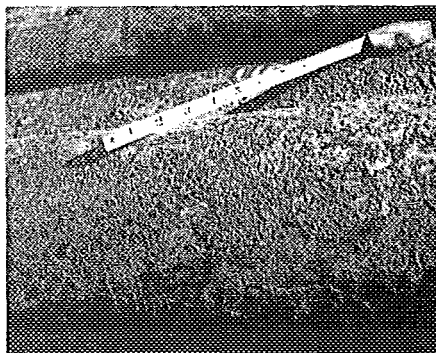
and results in the formation of protective calcareous deposits, Fig. 97. After this initial stage, the calcareous deposit and adequate protection can be maintained by reduced current densities.

The need for cathodic protection can be estimated by past corrosion experience or by a corrosion survey. Such a survey can determine the presence and location of "hot spots" or anodic areas on the pipe. With this knowledge and with data on soil resistivities of the areas involved, a cathodic protection system can be designed. This design is largely an art. It is not yet possible to give a fixed set of rules.

A simple method of obtaining a degree of protection from corrosion without making an expensive survey is that of hot-spot protection. In this method, an anode is installed every time a leak is repaired. This eventually provides protection for the worst areas. This technique can be improved somewhat by predicting the hot spots, based on terrain. In other words, they are likely to occur at low damp spots, under roads, and under ditches or streams.

In all cathodic protection installations it is important that anodes be properly installed so that there is a minimum electrical resistance between the anode and the surrounding soil. Where possible, anodes should be placed in areas of low soil resistance such as in old mud pits. A low resistance material is usually packed around the anode to serve as backfill. A typical installation is shown in Fig. 98 and 98a.

A major problem when using rectifiers as a power source (previously illustrated in Fig. 95), is that of interference due to unprotected lines. It can be seen that the foreign line receives protection where current enters the pipe, but accelerated corrosion occurs where the current leaves the foreign line. If a proper metallic connection is placed between the protected and unprotected lines, this problem does not occur. Of course this means both structures are then receiving cathode currents, and the current required for adequate protection is correspondingly increased.

68   CORROSION OF OIL- AND GAS-WELL EQUIPMENT
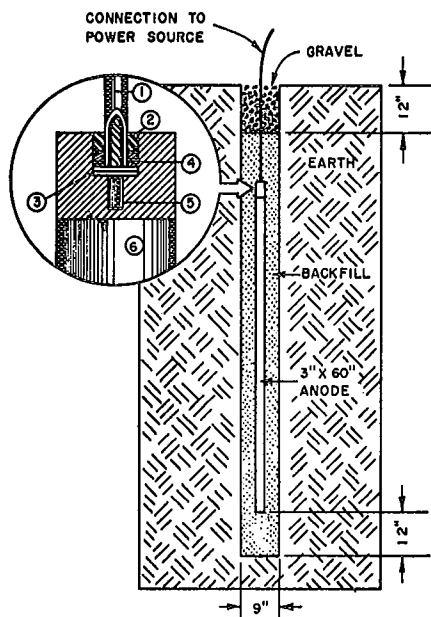
Fig. 98 (left) — Typical Graphite Anode
Installation

① INSULATED, WATERPROOF CABLE

② RUBBER GASKET

③ COPPER DRIVING WASHERS

④ WATERPROOF SEAL

⑤ KNURLED COPPER FERRULE SOLDERED
   TO CABLE

⑥ ROD IMPREGNATED AGAINST MOISTURE
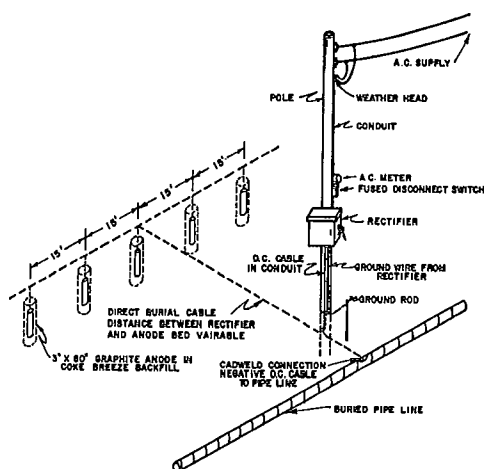
Fig. 98a (right) — Typical Rectifier Installation

Another problem with cathodic protection is that low current densities may protect most of the total area of a piece of pipe, but may be unable to handle a very severe damage occurring over a small area. An example is welded pipe which is subject to a special type of attack called "seam corrosion," Fig. 99. Once this attack starts, it is very difficult to stop with usual levels of protective current because current enters the crevice with more difficulty than in flat areas. In the same fashion,
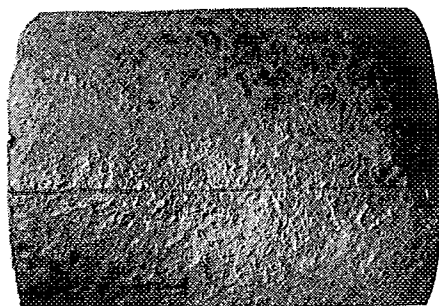
Fig. 99 — Seam Corrosion in Electric-resistance-welded Pipe is Very Difficult to Stop by Cathodic Protection

cathodic protection at low current densities will not always protect the steel under corrosion tubercules. In well casing under cathodic protection, it can be shown that currents ranging from 1 to 5 amp are sufficient to remove most corrosion cells. However, there is no assurance that a few very small but powerful cells will not give failures at a rapid rate. This question is of great importance but can be adequately answered only after extensive field testing.

In the discussion thus far, the use of cathodic protection for flow lines and well casing has been discussed. Other valuable uses for cathodic protection can be briefly outlined.

1. *Offshore Structures.* It is believed that almost every offshore structure used in the petroleum industry is now under cathodic protection, since it is relatively easy to polarize steel in sea water. The calcareous deposit formed by polarization is effective in reducing the exposed area of steel so that there is little advantage in coating the submerged portion of the structure. Typical installations are shown in Figs. 100, 101, and 102.

2. *Surface Vessels.* Surface vessels such as water tanks are often protected against internal corrosion by oilfield brines by cathodic protection (Figs. 103, 104, and 105). An applied current of 10 to 40 milliamperes per square foot has been found to maintain adequate protection, in most cases, provided initial polarization has been accomplished. Any inlets or outlets on the vessel will not be protected since the applied current cannot be thrown into a hole except for a distance of about three times the diameter of the hole concerned.

ECONOMICS OF CATHODIC PROTECTION

Cathodic protection has found widespread application for the mitigation of external and internal electrochemical corrosion. In most cases, cathodic protection is one of the least expensive corrosion mitigation methods when the alternatives such as continuous chemical injection, and partial replacement of equipment are considered.

70   CORROSION OF OIL- AND GAS-WELL EQUIPMENT
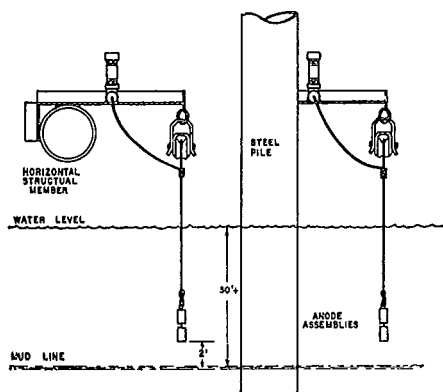
Fig. 100 — Typical Anode Installation Offshore
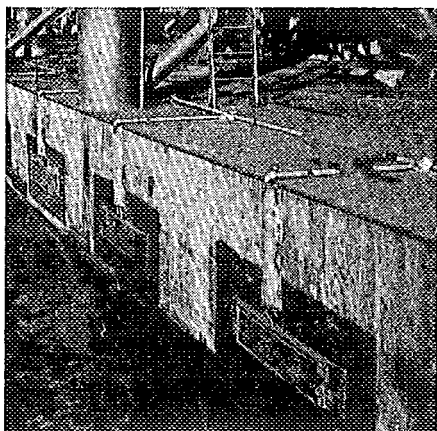
Fig. 101 — Graphite Anode Assembly on Sub-
mersible Hull of Drilling Barge — Rectifiers on
Upper Deck
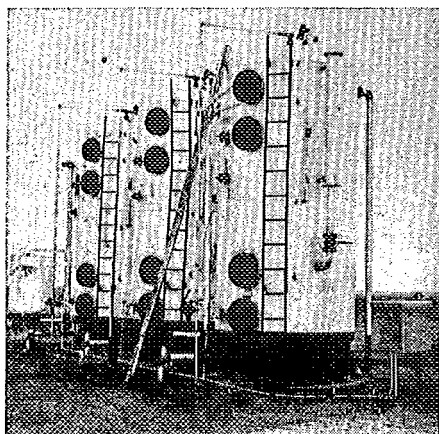
Fig. 102 — Rectifier-graphite Anode Installed on
Water-treating Vessels
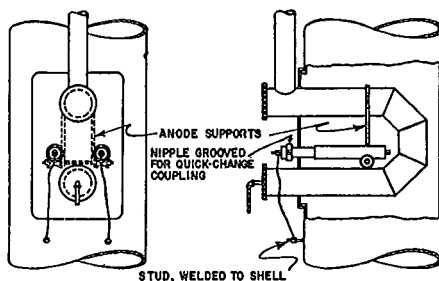
Fig. 103 — Typical Anode Installation in
Heater-treater
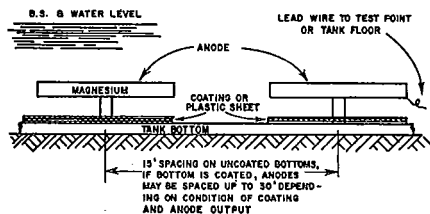
Fig. 104 — Typical Anode Installation in the
Bottom of an Oil-storage Tank
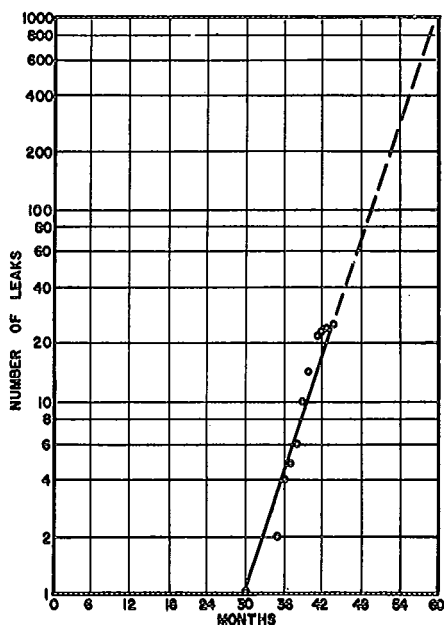
Fig. 105 — Failure Frequency of Buried Line

APPENDIX

PART 1: GLOSSARY OF TERMS

ABSORPTION — Soak up as a sponge takes up water.

ADSORPTION — The accumulation of a thin layer of molecules of gas or liquid on a solid surface.

AEROBIC — With atmospheric oxygen present.

ALLOY — A metal composed of two or more elements, at least one of which has good metallic properties.

ANAEROBIC — With atmospheric oxygen absent.

ANODE — The portion of a corrosion cell which corrodes. Oxidation always occurs at anode.

ATOM — The smallest particle of matter which can enter into chemical combination, i.e., iron (Fe), oxygen (O), hydrogen (H), carbon (C), chlorine (Cl).

AUSTENITIC — A non-magnetic (face-centered cubic) state of iron or an iron alloy.

BAND-STRAPPING — A method of attaching plastic or metal sheeting to a cylindrical structure by use of metal bands which encircle the sheeting and secure it in place.

BIMETALLIC CELL — A corrosion cell in which dissimilar metals are connected together electrically both with a metallic path and with a liquid which is corrosive to at least one of the metals.

BRASS — An alloy of copper (60 percent or over) and zinc.

BRONZE — An alloy of tin (usually under 12 percent) and copper. Frequently used as a name for brass.

CALCAREOUS COATING — A chalky coating of calcium carbonate and/or magnesium hydroxide.

CAPILLARY WATER RISE — The rise of water in a loosely compacted material such as a sand fill, due to capillary forces.

CAST IRON — An alloy of iron and about 2 to 4 percent carbon.
  a. *Grey cast iron:* The graphite (carbon) is present as flakes. This makes a fracture appear grey.
  b. *White cast iron:* The carbon is present as carbides. With no graphite to color it, a fracture appears a metallic white.

CATHODE — The portion of a corrosion cell which does not corrode. Reduction always occurs at the cathode.

CLADDING — A process for covering one metal with a thinner sheet of another to obtain increased corrosion resistance or other desirable properties of the thinner material.

CONCENTRATION CELL — A corrosion cell caused by two areas of metal being exposed to (localized) environments of different concentrations of chemical species present. Examples include: *Metal ion:* A corrosion cell in which a potential difference is produced by a difference in concentration of metal ions. *Oxygen:* A corrosion cell in which a potential difference is produced by differences in oxygen concentration. Region of low oxygen concentration is the anode or corroding area.

COPOLYMER — A molecule formed when two or more unlike polymers are linked together.

CORROSION-FATIGUE FAILURE — Failure of a metal exposed to repeated loading in corrosive service.

CORROSION PRODUCT — The material which results from a metal combining with its corrosive environment.

CORROSION AGENT — Any agent causing corrosion.

COUPON — Small metal strips which are exposed to corrosive systems for the purpose of determining nature and severity of corrosion.

CREEP — The gradual deformation of metals or plastics under loads applied for a long time.

CUPRONICKEL — An alloy of copper (70 percent or over) and nickel.

DEPOLARIZE — To increase rate of corrosion reaction by removing a polarizing corrosion product.

ELECTROCHEMICAL — Chemical changes associated with flow of electric current.

ELECTROLYTE — A liquid or soil capable of conducting electric current.

FATIGUE — Failure of a metal under repeated loading.

FREE MACHINING — A characteristic of being machined easily. For example, this may be accomplished by adding sulfur to steel or lead to brass.

GALVANIZE — To coat a metal with zinc.

HOLIDAYS — Areas of metal that have been missed by one or more applications of a coating material, resulting in pinholes or reduced film thickness.

HYDROLYSIS — A reaction involving the splitting of water into H+ and OH— to form a weak acid or base or both.

INHIBITION — The diminishing of the rate of a chemical reaction to retard corrosion.

ION — Electrically charged particle, atom, or radical.

IR — Letter symbols of current *(I)* and resistance *(R)* as used in Ohm's law *(E=IR)*.

MEGGER INSTRUMENT — A device for measuring resistances. Used for determining coating insulation or electrolyte resistance.

MELT — To convert a solid substance into the liquid state through a process of heating, or a quantity of metal melted at a single operation.

METALLURGY — The art and science of extracting metals from their ores, refining them, and preparing them for use. Can also be the technical details of a metal and often deals with behavior of metals under various environmental conditions.

MIL — One thousandth of an inch (0.001 in.)

MOLECULE — The smallest particle of any substance that can exist free and still exhibit all the properties of the original substance.

MONEL — A trademark name of an alloy of about 70 percent nickel, 30 percent copper.

MPY — Measure of corrosion penetration rate in mils per year.

ORGANIC AMINE INHIBITOR — A chemical consisting of carbon, hydrogen, and nitrogen which reduces corrosion rates.

OXIDATION — *1*, Chemically combining with oxygen to form an oxide; or *2*, electrochemically, as the loss of electrons at the anode of a corrosion cell.

PEARLITIC — Alternate parallel platelets of iron and a microstructural arrangement having iron carbide in one grain. May also refer to a steel with a preponderance of such carbide arrangements.

pH — A symbol which signifies the concentration of hydrogen ion. The lower the pH (more acidic), the higher the concentration of hydrogen ions. The higher the pH (more basic), the lower the concentration of hydrogen ion.

PLASTICS — Large group of organic, synthetic or processed materials used for coating; or that are molded, cast, or extruded and used for making structural items.

Acetate Butyrate — Produced by reacting cellulose with acetic and butyric anhydride.

Epoxy — Produced by reaction between epichlorohydrin and bisphenol H to A.

Phenolic — Produced by reacting formaldehyde and phenol.

Polyester — Produced from polybasic alcohols and polybasic acids.

Polyethylene — Composed of polymers of ethylene.

Polyurethane — Produced from propionaldehyde, trimethylolpropane, propionic acid, and ammonia.

Styrenes — Polystyrene is produced by polymerizing styrene. A butadiene-styrene copolymer is formed by reacting butadiene and styrene.

Vinyl — Polyvinyl chloride (PVC) is produced by the addition-type polymerization of vinyl chloride.

POLAR ORGANIC — A compound of carbon which will adsorb on a solid surface.

POLARIZE — Retard an electrochemical corrosion reaction by deposition of a corrosion product.

POLYMER — A compound formed by linking of a molecule with itself to form a very long molecule.

POLYPHOSPHATES — A phosphate compound used for water stabilization and corrosion inhibition.

POTENTIAL — Voltage under standardized conditions. The driving force for electric current to flow between two metals, between two areas of the same metal, between anode and cathode or between areas of oxidation and reduction reactions, measured in volts.

POTENTIOMETERS — An instrument used to measure electric potentials.

REFERENCE ELECTRODE — A standard cell of known voltage used for making voltage measurements of a corrosion cell. Calomel and copper sulfate are common reference electrodes.

ROCKWELL HARDNESS — A numerical value which expresses the resistance of a material to indentation by a standard shaped indentor and standard load. This correlates directly with strength.

SILICATE — A compound containing $SiO_3 =$ which may be used for the prevention of metal corrosion caused by oxygen.

SINTERED CARBIDES — Most commonly, iron, chromium, or tungsten carbides bonded together with nickel or cobalt.

SODIUM CHROMATE — Na_2CrO_4; an inorganic water-soluble chromium compound useful as an inhibitor of iron corrosion caused by oxygen.

SODIUM DICHROMATE — $Na_2Cr_2O_7$; sodium chromate in acid systems.

SODIUM NITRITE — $NaNO_2$; an inorganic water-soluble chemical useful as an inhibitor of iron corrosion caused by oxygen.

SOLUBLE OILS — Compounds which may possess corrosion-inhibition properties, are dispersible in water, and are soluble in oil.

SPALLING — Flaking off in small chips.

SPHEROIDIZED CARBIDES — Iron carbides in steel present as tiny round spheres.

STAINLESS STEEL — *a. Non-magnetic (austenitic):* An alloy of chromium (over 16 percent), nickel (over 7 percent), and iron. Manganese can be used to partially replace nickel. *b. Magnetic (ferritic):* An alloy of chromium (over 11 percent) and iron.

STEEL — An alloy of iron and carbon having two main constituents — iron and iron carbide.

STRIKE PLATE — Extra piece of metal to protect the bottom of a tank from plumb-bob at end of gager's tape.

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PART 3: OIL WELL PUMPS

Pumps, although they represent only a small portion of the equipment for a well, can be a considerable source of maintenance expense. Corrosion in the pumps can be controlled by the use of inhibitors, by the use of corrosion-resistant materials, or, better, by use of the combination of these. Inhibitors have been discussed in some detail. There is a whole host of metals in use, and the identity of many of these is hidden under trade names. The subject of metals is best discussed in terms of increased corrosion resistance and remedies for various types of damage.

Grey cast iron and common steel for plungers, barrels, and liners can be used when corrosion is very mild. Even within the range of these materials corrosion can vary considerably. The pearlitic materials have better corrosion resistance in sweet uninhibited wells than do either the very low-carbon materials or the steels with a well tempered structure (with spheroidized carbides). Nickel steels have somewhat increased resistance to pitting in uninhibited sour wells. Although chromium has good resistance to well fluids, chrome plate cannot be relied on entirely because it is somewhat porous. In addition, adhesion of chrome plate is a problem and should always be suspected when the plate comes off in patches. Chrome plating will generally fail on pumps if acid is dumped in the well. A still higher degree of corrosion resistance can be obtained using the very hard cast irons. The corrosion resistance of these increases with increasing proportion of cementite — the compound of iron and carbon. Copper base alloys and Monel metal have very good resistance to corrosive well fluids except when oxygen is present.

Wear is also an important factor in oil well pump barrels and plungers. Common steel has comparatively poor resistance, and chrome plate is almost always necessary to make it wear satisfactorily. Cast iron has even better wear resistance, and it is possible to run cast iron against cast iron without galling. The white cast irons have the best resistance to sand wear of any materials.

A wide choice of materials is also available for balls and seats. Because of the great tendency to corrosion erosion (wire-drawing or cutting) the high-carbon — low-alloy steels are not widely used. The 12-percent chrome alloys are about the first step in terms of increasing corrosion resistance. If this has insufficient corrosion resistance, Type 440B or C stainless (high-carbon 16-percent chromium) should be used. Brass, beryllium bronzes, and nickel-base alloys have good corrosion resistance although they are somewhat soft and cannot always be used when pounding is severe or fluid columns are high. The sintered carbides — such as chromium, tungsten, and titanium carbides — have excellent corrosion and deformation resistance. For balls there is some advantage in using the light-weight carbides, such as chromium and titanium carbide, if the seat is being pounded out by the balls. Ceramic balls and seats, although they have excellent corro-

sion resistance, tend to break more readily than the carbides. Both carbides and ceramic materials have good resistance to sand conditions.

One other problem in steel balls and seats is hydrogen embrittlement. Especially if balls are frequently broken, this damage must be considered. The remedy generally is to go to the copper base, nickel base, or sintered carbide materials. Occasionally free machining steels, which have comparatively poor ductility, are used in oil well pump parts, and may be another cause of breakage. Given any choice, avoid the use of resulfurized steels because of poor corrosion resistance and reduced ductility, especially transverse ductility.

PART 4: SURVEY METHODS USED IN CATHODIC-PROTECTION STUDIES

Determining the need for cathodic protection requires special instrumentation and experience. A corrosion survey may be made by one of three methods. These are: *1*, structure-to-earth potential measurements; *2*, IR drop (current flow); and *3*, soil resistance measurements.

Potential Measurement

The potential of the structure (metal) being investigated as referred to earth along the structure is determined. The potentials usually range from a few millivolts to a few volts. In order to obtain accurate measurements of the potentials, it is necessary to use instruments having a high sensitivity. Generally, high resistance (greater than 10,000 ohms per volt) millivoltmeters may be used satisfactorily. Also, potentiometers and vacuum-tube voltmeters have been successfully used. Also needed is a suitable, nonpolarizing electrode and a contact bar. Generally, a copper — copper sulfate electrode is used as the reference electrode.

In making the survey, the structure is contacted by risers, through valve boxes, or by use of the contact bar. It is extremely important that a good low resistance electrical contact is established to the buried structure. The negative post of the voltmeter is connected through suitable leads to the pipeline contact, and the positive post is connected to the reference electrode. If a copper — copper sulfate electrode is used, the pipe will exhibit a negative polarity. This is shown schematically in Fig. 106. The potential of the structure is taken with the electrode firmly embedded in the earth directly over the structure. If possible, the electrode should be buried in a shallow hole. The structure-to-earth potential *(P/S)* is recorded. This procedure is repeated at suitable intervals throughout the entire system under study. Areas of more negative potential indicate anodic or corroding areas.

A modification of the technique is widely used, particularly on shallow buried bare pipe, and is called the surface potential method. This method requires a high resistance voltmeter and two reference electrodes.

The two copper sulfate electrodes should be checked at the start and should read within 2 millivolts of each other. The electrodes are placed directly over the center of the pipe at a suitable distance apart, and the potential difference between the two electrodes is read on the voltmeter. This procedure is repeated over the entire length of the structure. The method is shown schematically in Fig. 107. The method determines the flow of current *through the earth*. The potential of the readings obtained is plotted against distance along the pipe and a "hot spot" or anode is indicated at the point of potential reversal or where current leaves the pipe.

Dependent upon the type of pipe, the service, and the cost of leak repair, cathodic protection is applied when potential differences along the line exceed 20 to 30 millivolts.
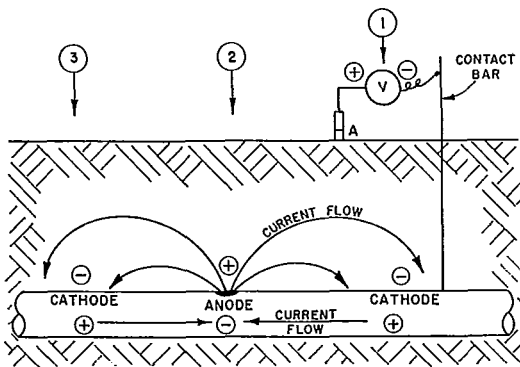
Fig. 106 (left) — Pipe-to-Soil Potential Measurement

Method of measuring pipe-to-soil potential with contact bar, voltmeter V and reference electrode A. Note polarity in soil and in pipe. *P/S* potential obtained at 1 and 3 will be more cathodic (less negative) than that obtained at anodic (corroding) area at 2.

Fig 107 (right) — Surface Potential Method

Surface potential method for determining corrosion. Electrodes A and B are connected through voltmeter V and the Δ potential is measured. The reading will become more positive as station 2 is approached, indicating an anodic or corroding area. Note polarity in both pipe and soil.
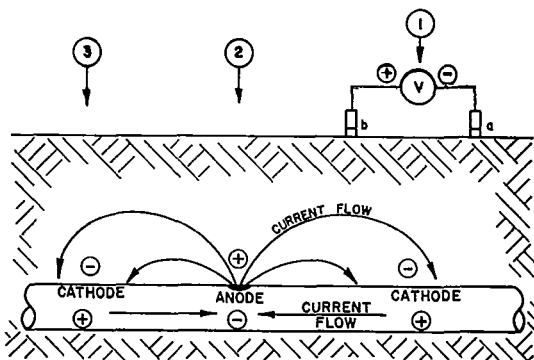
IR Drop (Current Flow)

The flow of direct current in the pipe is determined. The area or location where current flows from the structure to the earth is where corrosion would be expected. The magnitude of current provides an approximation of loss of metal per year which, if concentrated over a small area, would indicate early failures; if spread over a large area, corrosion may not be serious.

Corrosion may be occurring in the absence of direct current flow on the structure. There may be serious local cell corrosion occurring between test stations that is not detected by this measurement.

In the method two contact bars, a low resistance millivoltmeter, and suitable leads are required. The low resistance voltmeter should have high sensitivity, as IR drops as low as 1 millivolt may be encountered.

There are two important factors to consider if measurements within practical engineering accuracy are to be obtained. These are:

a. The resistance of the test leads and contact with the structure must be low, on the order of 1 percent, compared to the internal resistance of the millivoltmeter. If this is not feasible, corrections must be applied to the readings for lead and contact resistance.

b. Where the IR drop is 1 millivolt or less, the effect of thermo potentials may need to be considered.

The technique of the measurement is illustrated in Fig. 108. The pipe is contacted with probe bars at suitable intervals. The differential potential is then measured between the two contacts. Knowing the resistance of the pipe, current flow can be calculated from the formula:

$$I = E/R$$

Wherein: I is current in amperes; E is potential in volts; and R is resistance in ohms.

Resistance values for various size pipe are shown in Table 4-1.

It should be noted that current flow *in the pipe* is determined. As shown in Fig. 108, the anodic area in the pipe will be at the point of most negative potential.
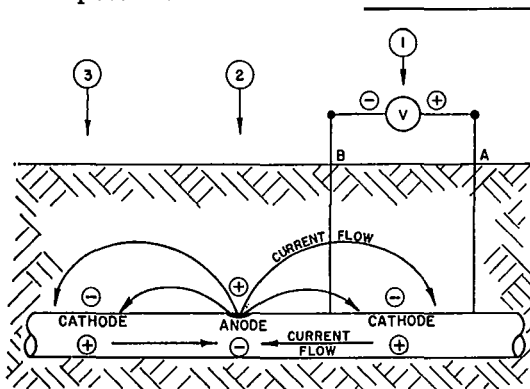

Fig. 108 — Current-flow Method (IR Drop).

Measuring IR drop in pipe to determine direction and amount of current flow. Δ potential is measured between contact bars *A* and *B* by low-resistance millivolt meter *V.* Current flow in the pipe is from + to − so anode will be at the most negative point in the pipe.

TABLE 4-1

Resistance and Current Data for Steel Pipe*

(From Bureau of Standards *Tech. Paper 355*)

Nominal Inside Diameter, In.	Standard			Extra-strong		
	Weight, Lb per Ft	Resistance, Microhms per Ft	Current for 1 Milli-volt on 1. Ft, Amp	Weight, Lb per Ft	Resistance, Microhms per Ft	Current for 1 Milli-volt on 1. Ft, Amp
1	1.68	129.0	7.8	2.17	100.0	10.1
1.25	2.27	95.0	10.5	3.00	72.0	13.9
1.50	2.72	79.0	12.6	3.63	60.0	16.8
2	3.65	59.0	16.9	5.02	43.0	23.3
2.50	5.79	37.3	26.8	7.66	28.2	35.5
3	7.58	28.5	35.1	10.25	21.1	47.5
3.50	9.11	23.7	42.2	12.51	17.3	58.0
4	10.79	20.0	50.0	14.98	14.4	69.0
4.50	12.54	17.2	58.0	17.61	12.3	82.0
5	14.62	14.8	68.0	20.78	10.4	96.0
6	18.97	11.4	88.0	28.57	7.6	132.0
7	23.54	9.2	109.0	38.05	5.7	176.0
8	24.70	8.7	114.0	43.39	4.98	201.0
8	28.55	7.6	132.0			
9	33.91	6.4	157.0	48.73	4.43	226.0
10	31.20	6.9	145.0	54.74	3.94	254.0
10	34.24	6.3	159.0			
10	40.48	5.3	188.0			
11	45.56	4.74	211.0	60.08	3.59	278.0
12	43.77	4.93	203.0	65.42	3.30	303.0
12	49.56	4.36	230.0			
13	54.57	3.96	253.0	72.09	3.00	334.0
14	58.57	3.69	271.0	77.43	2.79	359.0
15	62.58	3.45	290.0	82.77	2.61	383.0

*National Tube Co. tables, 1918. Resistivity = 215.8 microhms (ft-lb).

Resistance Measurements

Since, generally, current flow to and from the pipe will occur at the areas of lowest earth resistance, it is logical to assume that low resistance areas could be anodic. This method then determines only the opportunity for corrosion as related to earth resistance and the location where such corrosion would be expected. It does not indicate whether or not corrosion is occurring.

The technique is one of determining the resistance of the earth at preselected areas along the pipeline. The resistance may be determined by use of the four pole megger instrument (Vibroground) or single point probes, such as the Sheppard cane. Actual resistance values alone have little meaning. The significance of the survey is in the differences in resistance along the line. Some companies have selected 2,000 ohm-centimeters as the suspect value; i.e., resistances below this value, corrosion is expected.

The results of the survey are used to select areas for installation of protective measures.

In all of the foregoing methods it should be stressed that the data are generally relative and the actual need for cathodic protection will depend upon the magnitude of the potential differences or current flow from point to point along the line, whether the line is bare or coated, and upon the cost of leak repair.

Qualitative Field Test for Iron Sulfide on Steel Equipment

Apparatus
  1—4-oz. dropper bottle.

Solutions
  15-percent hydrochloric acid containing 1.0 percent sodium arsenite (NaAsO₂) and 0.05 percent liquid detergent.

Procedure
  A drop of the acid solution is placed on the equipment or scale being examined. If a bright yellow precipitate of arsenic sulfide is formed, the sample contained iron sulfide.

Since some iron will be dissolved by the acid, a yellow-orange solution may result. This should not be mistaken for the yellow precipitate formed by the sulfide.

Caution
  This test should be used *only on steel equipment*. Do not use on aluminum, zinc coatings or metal plating, because poisonous fumes may be formed.

Simplified Procedure for the Field Determination of Hydrogen Sulfide in Water

Aparatus

    1—100-ml graduated cylinder.
    1— 10-ml graduated pipette.
    1—250-ml Erlenmeyer flask.

Solutions

    1/10 normal iodine.
    Hydrochloric acid, dilute
      (1 part acid — 4 parts water).

Starch solution prepared by thoroughly wetting approximately ¼ teaspoonful of starch (preferably arrowroot starch) with a little cold water, and then adding 100 ml of boiling water with constant stirring. The mixture is allowed to cool and the clear solution is poured off. Use only fresh solution.

Procedure

    Accurately measure in a graduated cylinder a suitable quantity of the water, as determined by a preliminary titration, to consume 5 to 10 ml of iodine. The quantity will usually be from 25 to 100 ml. Transfer the measured sample to the Erlenmeyer flask, add 2 to 3 ml of the dilute acid, about 1 ml of starch, and sufficient distilled water to bring the total volume to approximately 100 ml, if less than 100 ml of sample is used. Titrate to the blue end point with iodine.

    The iodine is added from the graduated pipette and the flask should be swirled constantly during the titration.

    The procedure of measuring and transferring the sample, and adding the acid and starch should be carried out as quickly as possible. When water is added to bring the volume to 100 ml, as indicated, the distilled water and the acid may be placed in the flask prior to measuring the sample, in order to save time. If possible, make several determinations and take the average.

Calculation

$$\frac{\text{Ml of 1/10 N iodine consumed} \times 1704}{\text{ml of sample}} = \text{parts per million } H_2S \text{ in the sample}$$

84   CORROSION OF OIL- AND GAS-WELL EQUIPMENT

Field Method for Determination of Iron (Ferrous) in Sweet Oilfield Waters

Direct determination of dissolved iron in water can be made at the well head or separator.

Apparatus
    1–100-ml graduated cylinder.
    1–250-ml Erlenmeyer flask.
    1–5-ml graduated pipette.

Solutions
    0.01 normal potassium dichromate.
    Indicator and acid mixture.

The indicator solution is made up by dissolving 0.15 grams of sodium diphenylamine-p-sulfonate in a quantity of water and then diluting to 60 ml with distilled water. The acid solution is made up by mixing 150 ml of sulfuric acid (sp. gr. 1.84) and 150 ml of phosphoric acid (sp. gr. 1.7) and then diluting to 1 liter with distilled water.

Procedure
The collection of a fresh sample is imperative. If collected from the separator, the separator should first be drained of all water, and then a fresh sample of water collected. The determination of iron can either be made immediately upon obtaining the sample or within a 16-hour period, if the acid mixture is added as soon as the sample is taken.

To 100 ml of water measured in the 100-ml cylinder, add approximately 1 ml of the indicator solution and 15 ml of the acid solution. Titrate the water with the potassium dichromate, adding it dropwise from the pipette, gently swirling the flask through the test. The end point is reached when a permanent purple color is obtained.

Calculation
The number of milliliters of 0.01 normal* potassium dichromate added, multiplied by 5.6 is the iron (ferrous or soluble) content in parts per million (ppm).

If the iron content of the sample is zero, no purple color or end point is reached.

Another method suitable for field analysis for determination of iron may be found in the appendix of the NGAA book, *Condensate Well Corrosion.*

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*If the iron content is high (above 25 ppm), 1/10 normal potassium dichromate may be used. The factor 5.6 then become 56.

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