Corrosion in the Oil Industry

Most metals exist in nature as stable ores of oxides, carbonates or sulfides. Refining them, to make them useful, requires energy. Corrosion is simply nature's way of reversing an unnatural process back to a lower energy state. Preventing corrosion is vital in every step in the production of oil and gas.

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Corrosion costs US industries alone an estimated \$170 billion a year. The oil industry, with its complex and demanding production techniques, and the environmental threat should components fail, takes an above average share of these costs.[1]
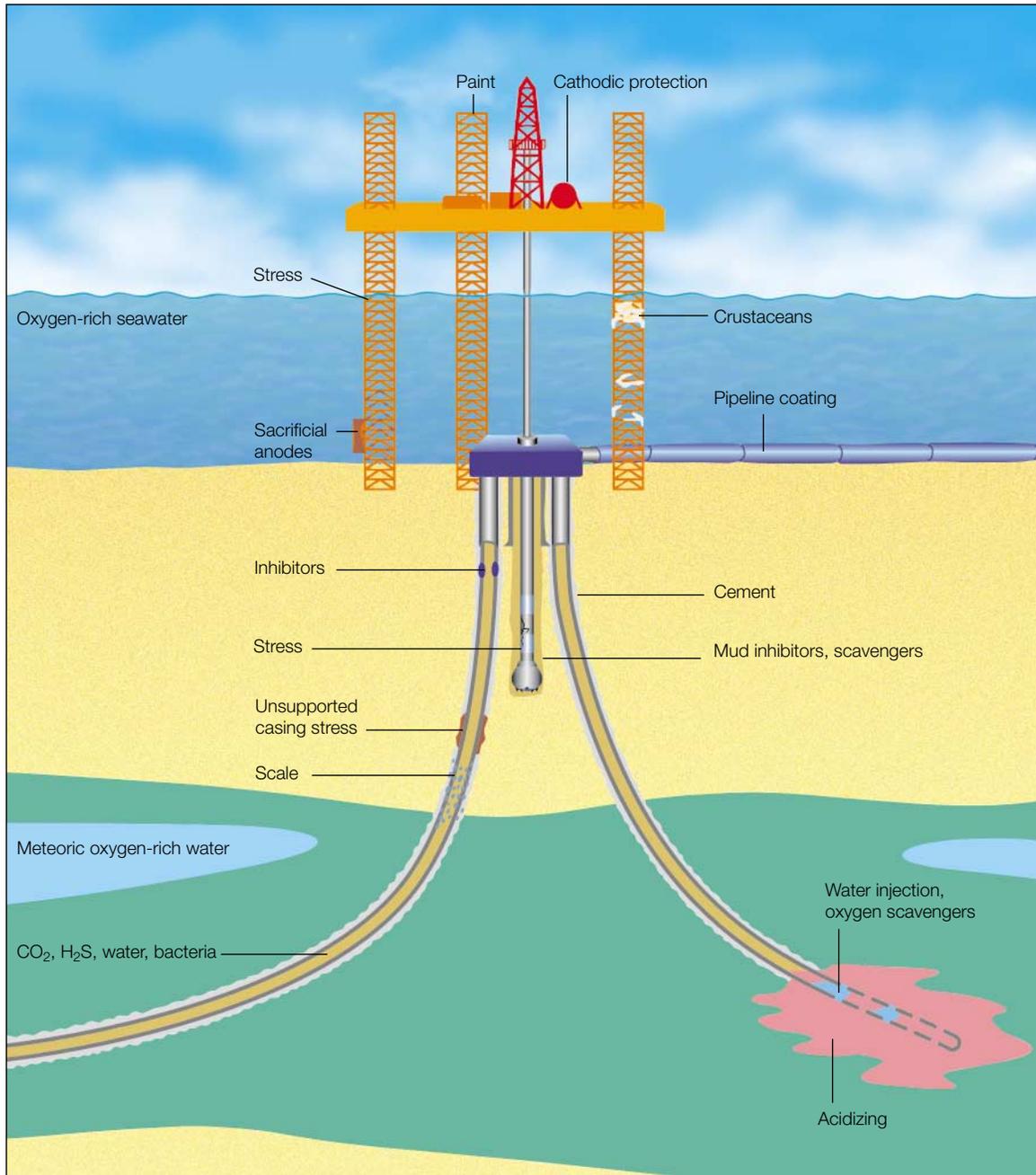
Corrosion—the deterioration of a metal or its properties—attacks every component at every stage in the life of every oil and gas field. From casing strings to production platforms, from drilling through to abandonment, corrosion is an adversary worthy of all the high technology and research we can throw at it.

Oxygen, which plays such an important role in corrosion, is not normally present in producing formations. It is only at the drilling stage that oxygen-contaminated fluids are first introduced. Drilling muds, left untreated, will corrode not only well casing, but also drilling equipment, pipelines and mud handling equipment. Water and carbon dioxide—produced or injected for secondary recovery—can cause severe corrosion of completion strings. Acid—used to reduce formation damage around the well or to remove scale—readily attacks metal. Completions and surface pipelines can be eroded away by high production velocities or blasted by formation sand. Hydrogen sulfide [H_2S] poses other problems (*next page*). Handling all these corrosion situations, with the added complications of high temperatures, pressures and stresses involved in drilling or production, requires the expertise of a corrosion engineer, an increasingly key figure in the industry.

Because it is almost impossible to prevent corrosion, it is becoming more apparent that controlling the corrosion rate may be the most economical solution. Corrosion engineers are therefore increasingly involved in estimating the cost of their solutions to corrosion prevention and estimating the useful life of equipment. For example, development wells in Mobil's Arun gas field in Indonesia have been monitored for corrosion since they were drilled in 1977.

Production wells were completed using 7-in. L-80 grade carbon steel tubing—an H_2S-resistant steel—allowing flow rates in excess of 50 MMscf/D [1.4 MMscm/D] at over 300°F [150°C]. High flow rates, H_2S and carbon dioxide [CO_2] all contributed to the corrosion of the tubing. Laboratory experiments simulated the Arun well conditions, alongside continued field monitoring. These help find the most economical solution to the corrosion problem.[2] The results showed that the carbon steel tubing would have to be changed to more expensive chromium steel or to corrosion-resistant alloy (CRA).

Paint Cathodic protection

Stress

Oxygen-rich seawater

Crustaceans

Pipeline coating

Sacrificial anodes

Inhibitors

Cement

Stress

Mud inhibitors, scavengers

Unsupported casing stress

Scale

Meteoric oxygen-rich water

Water injection, oxygen scavengers

CO_2, H_2S, water, bacteria

Acidizing

Corrosion in every aspect of the oil industry. From generalized corrosion caused by oxygen-rich environments on marine structures to sulfide stress corrosion in hostile wells, the corrosion engineer is faced with a whole gamut of problems.

The Basic Corrosion Cell

By recognizing corrosion when it does occur, and by understanding the mechanisms involved, corrosion engineers may begin to eliminate corrosion by design.

The basic galvanic corrosion mechanism follows the principle of a battery. A typical battery requires two dissimilar metals connected together and immersed in an elec-

1. For a comprehensive reference book see:
   ASM Handbook Volume 13 Corrosion. Materials Park, Ohio, USA: ASM International, 1992.
   For an easier read:
   Jones LW: *Corrosion and Water Technology for Petroleum Producers.* Tulsa, Oklahoma, USA: OGCI Publications, 1988.
   Tuttle RN: "Corrosion in Oil and Gas Production," *Journal of Petroleum Technology* 39 (July 1987): 756-762.

2. Sutanto H, Semerad VAW and Bordelon TP: "Simulation of Future Wellbore Corrosion With Low Production Rate Field Tests," paper 571, presented at the Corrosion 91 NACE Annual Conference and Corrosion Show, Cincinnati, Ohio, USA, March 11-15, 1991.
   Semerad VAW and Sutanto H: "Wellbore Corrosion Logging of Deep Hot Corrosive Wells," paper OSEA 90141, presented at the 8th Offshore South East Asia Conference, Singapore, December 4-7, 1990.
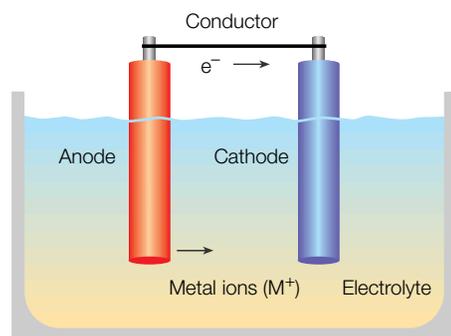   Asphahani AI, Prouheze JC and Petersen GJ: "Corrosion-Resistant Alloys for Hot, Deep, Sour Wells: Properties and Experience," *SPE Production Engineering* 6, no. 4 (November 1991): 459-464.
   Farooqul MASZ and Holland S: "Corrosion-Resistant Tubulars for Prolonging GWI Well Life," paper SPE 21365, presented at the SPE Middle East Oil Show, Manama, Bahrain, November 16-19, 1991.
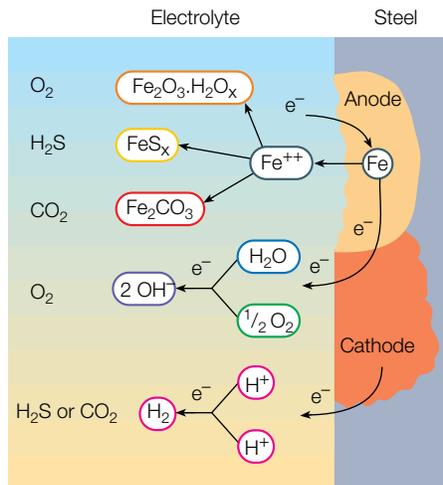
trolyte (*below*).[3] All metals have a tendency to dissolve or corrode to a greater or lesser degree. In this case, the metal with the greater tendency to corrode forms the negative pole and is called the anode.[4] When the two are connected, the other metal forms the positive pole, or cathode.

Loss of positive metal ions from the anode causes a release of free electrons. This process is called oxidation. The buildup of electrons generates an electrical potential, causing them to flow through the conductor to the cathode. At the cathode, excess electrons are neutralized or taken up by ions in the electrolyte. This process is called reduction. As long as reduction reactions predominate, no metal is lost at the cathode. The anode will continue to corrode as long as the electric circuit is maintained and the metal ions are removed from solution by combining with other elements to make up corrosion products.

Anodes and cathodes can form on a single piece of metal made up of small crystals of slightly different compositions. (They can be next to each other or separated by large distances–sometimes tens of kilometers.) The electrolyte may simply be water (*right*). For example, pure iron [Fe] in steel has a

□*Corrosion on a steel surface. At anodic sites, iron readily goes into solution as iron ions, Fe^{++}, which combine with oxygen, O_2, hydrogen sulfide, H_2S, or carbon dioxide, CO_2, depending on the constituents of the electrolytic fluid. These form corrosion products or scales as rust—iron oxide [$Fe_2O_3 \cdot H_2O_x$], iron sulfides [FeS_x] or iron carbonate [Fe_2CO_3]. While this is happening, the electrons migrate to the cathode. At the cathode surface, they reduce oxygenated water to produce hydroxyl ions [OH^-] or reduce hydrogen ions to produce hydrogen gas [H_2].*

□*Corrosion cell. The basic corrosion cell is formed by two dissimilar metals immersed in an electrolyte joined by a conductor. One electrode will tend to corrode more readily than the other and is called the anode. The anode loses positive metal ions to the electrolyte leaving free electrons and a net negative charge. At the other electrode, called the cathode, free electrons are taken up by ions in the electrolyte leaving a net positive charge. Free electrons can travel from anode to cathode along the conductor. The electrolyte then completes the circuit.*

tendency to dissolve, going into solution as Fe^{++}. As each Fe^{++} ion is formed, two electrons are left behind, giving that area of the metal a small negative charge. If nothing happens to remove Fe^{++} ions around the anodic site, the tendency to dissolve will diminish. In oil production, Fe^{++} ions are removed by reacting with oxygen [O_2], hydrogen sulfide, or carbon dioxide. The corrosion products are precipitates or scales of rust [Fe_2O_3], iron sulfides [FeS_x] or iron carbonate [Fe_2CO_3].

Excess electrons flow away from the anodic region to a site where they form a cathode, and where reduction occurs. Reduction of oxygenated water forms hydroxyl ions [OH^-]. If oxygen is not present, but CO_2 or H_2S is, then the dominant cathodic reaction is the reduction of hydrogen ions to produce hydrogen gas. If the electrolyte is salt water, chlorine gas is produced (see "Corrosion Mechanisms," *page 8*).

Identifying the Causes and Applying Controls

There are many sources of corrosion and many more methods of slowing the process down. This section looks at different parts of the industry and identifies typical corrosion problems and some of the solutions (*next page*).
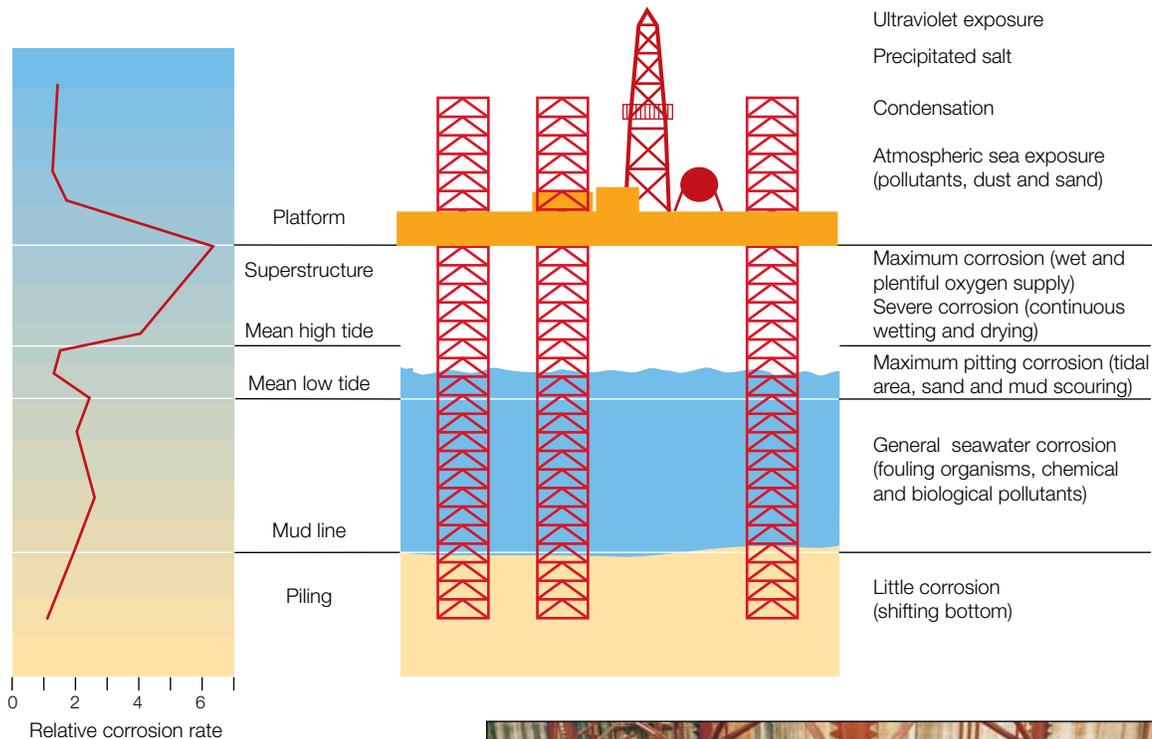
Offshore structures—On surface equipment, the simplest solution is to place an insulating barrier over the metal concerned. Offshore installations are often painted with zinc-rich primers to form a barrier against rain, condensation, sea mist and spray. The zinc primer not only forms a physical barrier, but also acts as a sacrificial anode should the barrier be breached.

Offshore structures are also protected in other ways.[5] The zone above the high tide mark, called the splash zone, is constantly in and out of water. The most severe corrosion occurs here. Any protective coating or film is continually eroded by waves and there is an ample supply of oxygen and water. Common methods of controlling corrosion in this zone include further coating and also increasing metal thickness to compensate for higher metal loss.

The part of the structure in the tidal zone is subjected to less severe corrosion than the splash zone and can benefit from cathodic protection systems at high tide.[6] Cathodic protection works by forcing anodic areas to become cathodes. To achieve this, a reverse current is applied to counteract the corrosion current. The current can be generated by an external DC source—impressed cathodic protection—or by using sacrificial anodes.

The rest of the structure—exposed to less severe seawater corrosion—is protected by cathodic protection. However, crustaceans and seaweed attach to the submerged parts adding weight that may increase stress-related corrosion. This mechanism occurs when the combined effects of crevice, or pitting, corrosion and stress propagate cracks leading to structural failure. However, a covering of life does restrict oxygen reaching metal, and so reduces corrosion.

Other forms of structural stress are also important. Low-frequency cyclic stress—resulting from factors such as waves, tides and operating loads—can allow time for corrosion within cracks as they are opened. Modeling and accounting for these stresses are therefore an extremely important part of corrosion prevention.[7]

Ultraviolet exposure

Precipitated salt

Condensation

Atmospheric sea exposure
(pollutants, dust and sand)

Platform

Superstructure

Mean high tide

Mean low tide

Maximum corrosion (wet and
plentiful oxygen supply)
Severe corrosion (continuous
wetting and drying)

Maximum pitting corrosion (tidal
area, sand and mud scouring)

General seawater corrosion
(fouling organisms, chemical
and biological pollutants)

Mud line

Piling

Little corrosion
(shifting bottom)

0   2   4   6
Relative corrosion rate

■ *Diverse corrosive environments attacking an offshore rig* (above, left)*. Sacrificial anodes on the leg and spud tank of Sedco Forex's Trident IV jackup rig* (left)*. Cathodic protection is a common way of combating corrosion; sacrificial anodes provide one method.*

The bottom of a jackup rig or production platform sinks into the seabed and is attacked by H_2S produced by sulfate-reducing bacteria (SRB).[8] However, cathodic protection also shields this part of the structure and, because of reduced oxygen supply, the protection current required tends to be less than for the rest of the rig.

Drillpipe corrosion—While a well is being drilled, stress is applied not only to the rig structure, but also to the drilling equipment. Drillpipe is probably the most harshly treated of all equipment. It is exposed to formation fluids and drilling mud, subjected to stress corrosion and erosion by cuttings. Joints of drillpipe are made from hardened high-strength steel and are likely to suffer from fatigue failures started by deep corrosion pits caused by oxygen, either from the mud itself or from being stacked wet. Drillpipe is sometimes coated internally, with baked resins or fusion bonded epoxies, to counteract corrosion. Once this coating has disappeared, however, corrosion can be rapid. A common area where drillpipe leaks or washouts occur is in the threaded drillpipe connections called tool joints. The

3. A corrosion cell may also be formed by having the same metal in two different electrolytes.

An electrolyte is a nonmetallic electric conductor. Current is carried through an electrolyte by the movement of charged atoms called ions. Negative ions have extra electrons and positive ions have lost electrons.

4. Confusion often arises over whether an anode is positive or negative, because in a driven cell, such as electroplating baths or vacuum tubes in old radios, the positive is the anode and the negative the cathode. In any battery, however, including a corrosion cell, the cathode has positive charge and the anode negative charge. At the anode, ferrous ions [Fe^{++}] leaving the surface leave a net negative charge, and the electrons flow through the metal to the cathode. At the cathode, hydrogen ions [H^+] discharge themselves to leave a positive charge and result in free hydrogen—polarization.

5. Watts RK: "Designing for Corrosion Control in Surface Production Facilities," paper SPE 9985, presented at the SPE International Petroleum Exhibition and Technical Symposium, Beijing, China, March 18-26, 1982.

Schremp FW: "Corrosion Prevention for Offshore Platforms," paper SPE 9986, presented at the SPE International Petroleum Exhibition and Technical Symposium, Beijing, China, March 18-26, 1982.

6. *ASM Handbook,* reference 1: 1254-1255.
Jones, reference 1: 75-78.

7. Barreau G, Booth G, Magne E, Morvan P, Mudge P, Pisarki H, Tran D, Tranter P and Williford F: "New Lease on Life for the 704," *Oilfield Review* 5, no. 2/3 (April/July 1993): 4-14.

8. Maxwell S: "Assessment of Sulfide Corrosion Risks in Offshore Systems by Biological Monitoring," *SPE Production Engineering* 1, no. 5 (September 1986): 363-368.

Corrosion Mechanisms

Corrosion encountered in petroleum production operations involves several mechanisms. These have been grouped into electrochemical corrosion, chemical corrosion and mechanical and mechanical/corrosive effects.

Electrochemical Corrosion

Galvanic Corrosion (Two Metal)—Two dissimilar metals in a conductive medium develop a potential difference between them. One becomes anodic, the other cathodic. The anode loses metal ions to balance electron flow. Because metals are made up of crystals, many such cells are set up, causing intergranular corrosion. Problems are most acute when the ratio of the cathode-to-anode area is large.

Crevice Corrosion—Much metal loss in oilfield casings is caused by crevice corrosion. This localized form of corrosion is found almost exclusively in oxygen-containing systems and is most intense when chloride is present. In the crevice, metal is in contact with an electrolyte, but does not have ready access to oxygen.

At the start of the reaction, metal goes into solution at anodic sites and oxygen is reduced to hydroxyl ions at cathodic sites. Corrosion is initially uniform over the entire area including the crevice. As corrosion continues in the crevice, oxygen becomes depleted and cathodic oxygen reduction stops. Metal ions continue to dissolve at anodes within the crevice, producing an excess of positive charges in solution. Negatively charged chloride (or other anions) now migrate to the developing anodes to maintain electroneutrality. They act as a catalyst, accelerating corrosion. At this point, crevice corrosion is fully established and the anodic reaction continues with ferrous ions [Fe++] going readily into solution (right).

Pitting corrosion is another form of crevice corrosion where a small scratch, defect or impurity
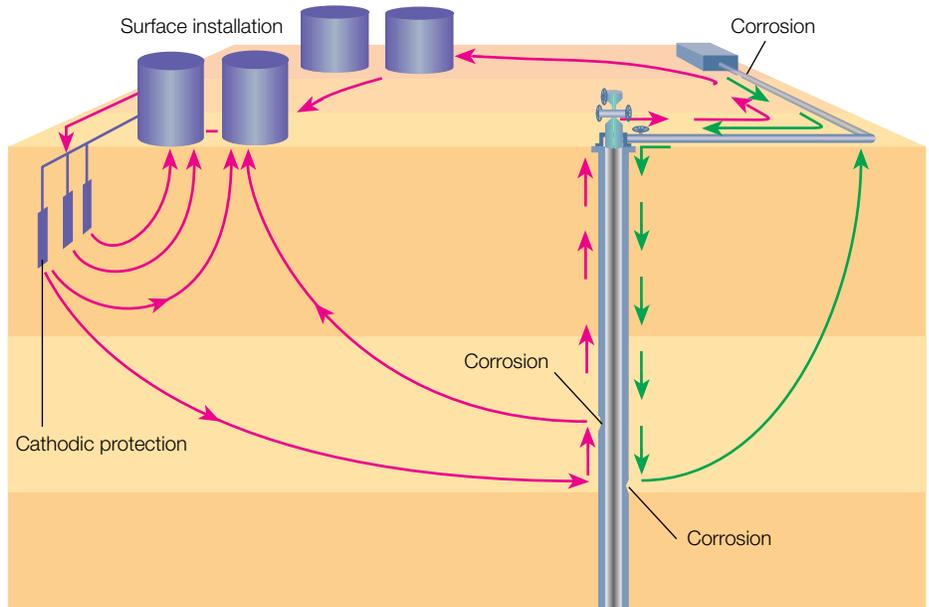
◻Stray-current corrosion. Current paths are shown between surface installation, electrical machinery, pipelines and a well. Current leaving the casing sets up an anodic area and corrosion.
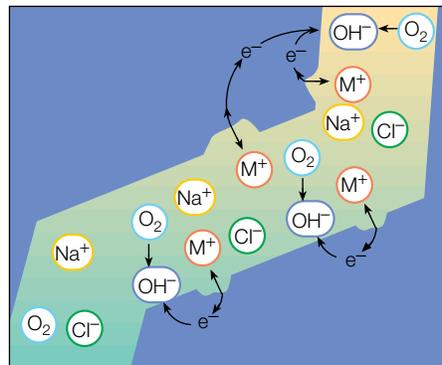
◻Crevice corrosion. This type of corrosion often starts at drillpipe joints, tubing collars or casing collars. The gap in the joint becomes devoid of oxygen and anodic. In salty water the corrosion is promoted by the migration of negatively charged chlorine ions [Cl⁻] to the crevice. These not only counteract the buildup of positive charges around the crevice, but also act as a catalyst accelerating the dissolution of metal [M⁺]. This ongoing process leads to a deep pit.

can start the corrosion process. Again, a buildup of positive charges occurs in a small pit on the metal surface. Chlorine ions from a saline solution migrate towards the pit. These, coupled with the formation of hydrogen ions, act as a catalyst causing more metal dissolution.

Stray-Current Corrosion—Extraneous AC and DC currents in the earth arriving at a conductor will turn the point of arrival into a cathode (above). The place where the current departs will become anodic, resulting in corrosion at that point. A DC current is 100 times more destructive than an equivalent AC current. Only 1 amp per year of stray DC current can corrode up to 20 lbm [9 kg] of steel. Cathodic protection systems are the most likely sources of stray DC currents in production systems.

Chemical Corrosion

Hydrogen Sulfide, Polysulfides and Sulfur—Hydrogen sulfide [H_2S] when dissolved in water, is a weak acid and, therefore, it is a source of hydrogen ions and is corrosive. (The effects are greater in deep wells, because the pH is further reduced by pressure.) The corrosion products are iron sulfides [FeS_x] and hydrogen. Iron sulfide forms a scale that at low temperatures can act as a barrier to slow corrosion. The absence of chloride salts strongly promotes this condition and the absence of oxygen is absolutely essential. At higher temperatures the scale is cathodic in relation to the casing and galvanic corrosion starts. In the presence of chloride ions and temperatures over 300°F [150°C] barnacle-type corrosion occurs, which can be sustained under thick but porous iron sulfide deposits (above, right). The chloride forms a layer of iron chloride [$FeCl_2$], which is acidic and prevents the formation of an FeS layer directly on the corroding steel, enabling the anodic reaction to continue. Hydrogen produced in the reaction may lead to hydrogen embrittlement.

Carbon Dioxide—Like H_2S, carbon dioxide [CO_2] is a weakly acidic gas and becomes corrosive when dissolved in water. However, CO_2 must hydrate to carbonic acid [H_2CO_3]—a relatively slow process—before it becomes acidic. The cor-
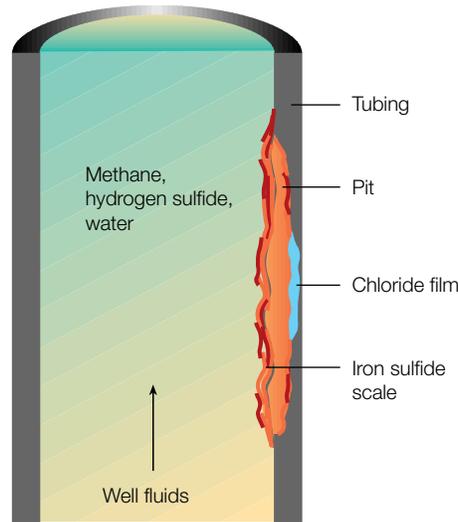
Barnacle-type corrosion. As tubing corrodes in a hydrogen sulfide and water environment, iron sulfide scale builds up. This is porous and is also cathodic with respect to the steel tubing. An intervening layer of iron chloride [$FeCl_2$] is acidic and prevents precipitation of FeS directly onto the steel surface. This establishes a pit-forming corrosion cell.

rosion product is iron carbonate (siderite) scale. This can be protective under certain conditions. Siderite itself can be soluble. Conditions favoring the formation of a protective scale are elevated temperatures, increased pH as occurs in bicarbonate-bearing waters and lack of turbulence, so that the scale film is left in place. Turbulence is often the critical factor in the production or retention of a protective iron carbonate film. Siderite is not conductive, so galvanic corrosion cannot occur. Thus corrosion occurs where the protective siderite film is not present and is fairly uniform over the exposed metal. Crevice and pitting corrosion occur when carbonic acid is formed. Carbon dioxide can also cause embrittlement, resulting in stress corrosion cracking.

Strong Acids (direct chemical attack)—Strong acids are often pumped into the wells to stimulate production by increasing formation permeability in the near wellbore region. For limestone formations, 5 to 28% hydrochloric [HCl] acid is commonly used. For sandstones, additions of hydrofluoric acid—normally up to 3%—are nec-

essary. In deep sour wells where HCl inhibitors lose effectiveness, 9% formic acid has been used. Corrosion control is normally achieved by a combination of inhibitor loading and limiting exposure time, which may range from 2 to 24 hr. If corrosion-resistant alloys are present (austenitic and duplex stainless steels), concern for stress-corrosion cracking (SCC) and inhibitor effectiveness may rule out the use of HCl. In addition to spent acid, other stagnant columns such as drilling and completion fluid, may also be corrosive.

Concentrated Brines—Dense halide brines of the cations of calcium, zinc, and, more rarely, magnesium are sometimes used to balance formation pressures during various production operations. All may be corrosive because of dissolved oxygen or entrained air. In addition, these brines may be corrosive because of acidity generated by the hydrolysis of metallic ions. Corrosion due to acidity is more severe with dense zinc brines. More expensive brines of calcium bromide are now often used at densities above 14 lbm/gal [1.7 gm/cm³] to avoid long-term exposure to zinc chloride [$ZnCl_2$] brines.

Biological Effects—The most important biological effect is the generation of H_2S by sulfate-reducing bacteria. These anaerobic bacteria metabolize sulfate ions (using an organic carbon source) and produce hydrogen sulfide. They can thus introduce H_2S into an H_2S-free system. Colonies of SRBs can also form deposits that lead to crevice corrosion with produced H_2S accelerating corrosion, because it is known to be an anodic stimulant. In low-flow rate systems, hard rust nodules or tubercles can form creating differential oxygen cells, which lead to crevice corrosion (below).
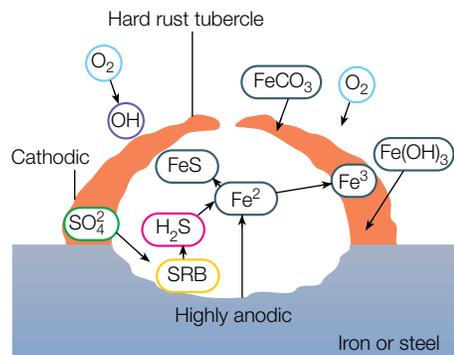
□Rust tubercle. Tuberculation is a complex localized process that forms a nodule-like structure. It often forms in a region of low fluid velocity where a deposit of sludge or rust can shield a part of the metal and reduce the oxygen available to that area. The portion of steel exposed to water with low oxygen concentration becomes anodic and corrodes at a faster rate than the rest.

Mechanical and Mechanical/Corrosive Effects
Cavitation—This type of metal loss—often grain by grain—is due to high-pressure shock waves, generated from the collapse of minute bubbles in high-velocity fluids impinging on nearby metal surfaces. Cavitation metal loss is usually found on pump impellers developing too low a suction pressure.

Erosion—This is direct metal removal by the cutting action of high-velocity abrasive particles. Erosion failures (washouts) are seen in drillpipe when leaks (loose connections or a corrosion fatigue crack) allow drilling mud to flow through the wall under high pressure. Erosion of flowlines at bends and joints by produced sand is probably the other most common occurrence of metal erosion in the petroleum industry.

Erosion Corrosion—When erosion removes the protective film of corrosion products, corrosion can occur at a faster rate. Erosion corrosion may play a role in CO_2 corrosion. Under mild flow conditions, sand may also cause erosion corrosion. This type of corrosion is also seen in anchor chains where corrosion between links proceeds quickly.

Corrosion Fatigue—This results from subjecting a metal to alternating stresses in a corrosive environment. At the points of greatest stress, the corrosion product film becomes damaged allowing localized corrosion to take place. Eventually this leads to crack initiation and crack growth by a combination of mechanical and corrosive action. Because of this combined action, corrosion fatigue is greater at low stress cycles that allow time for the corrosion process. Welded connections on drillships, drilling and production rigs and platforms are subject to this type of corrosion.

Sulfide Stress Corrosion—Production of hydrogen results from sulfide stress cracking (SSC). SSC occurs when a susceptible metal is under tensile stress and exposed to water containing hydrogen sulfide or other sulfur compounds—generally under anaerobic conditions. Corrosion cells generate FeS and atomic hydrogen. The amount of metal loss is small and the FeS layer thin. The layer of FeS promotes the movement of hydrogen into the metal, usually into impurities at the grain boundaries. Penetration of hydrogen into the body of the metal reduces ductility. Accumulations of hydrogen at imperfections generate tremendous pressure. For hard high-strength steel the combination of lack of ductility and internal stress superimposed on the tensile stress causes the metal to break and crack (right). Penetration of molecular hydrogen can also lead to blistering.

Chloride Stress Cracking (CSC)—While under tensile stress, austenitic stainless steels can fail by cracking when exposed to saline water above 200°F [95°C].

Stress Corrosion Cracking (combined with SSC, CSC and corrosion fatigue)—CSC is an example of a broad range of stress-corrosion cracking, defined as corrosion accelerated by tensile stress. This type of corrosion starts at a pit or notch, with cracks progressing into the metal primarily along grain boundaries.
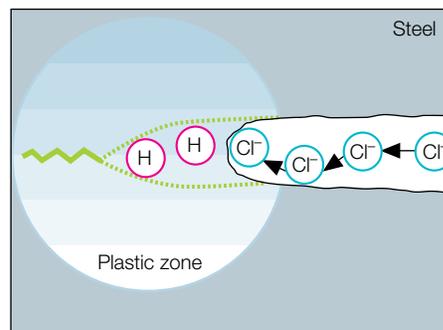
Hydrogen Embrittlement
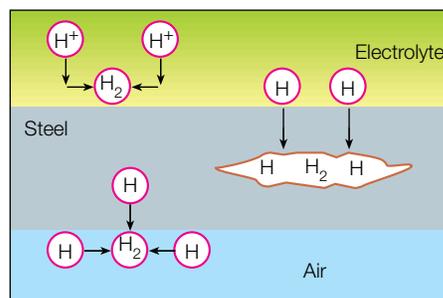
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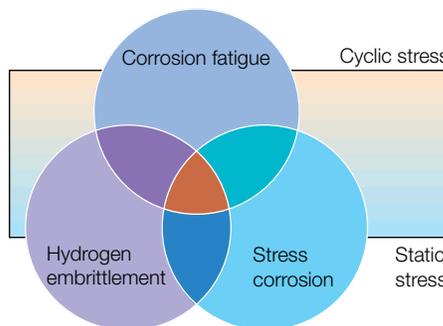
Stress Corrosion Cracking

□Hydrogen embrittlement and stress corrosion. When H_2S is present, corrosion cells generate FeS and atomic hydrogen. The layer of FeS promotes the movement of hydrogen into the metal (top), and accumulations generate tremendous pressure. This leads to embrittlement and, if combined with static or cyclic stress, can lead to failure of the metal by corrosion fatigue or stress corrosion (middle). Stress corrosion cracking (bottom) starts at a pit or crevice. The zone around the tip of the crevice becomes plastic under stress allowing a crack to develop. Chlorine ions, which act as a catalyst to corrosion, can migrate into the crack accelerating the process. The development of the crack within the plastic zone is another site for hydrogen embrittlement.

threads provide ideal places for crevice corrosion, which can also occur in scars left on the tool joints by makeup tongs. A special grease, commonly known as dope, lubricates the threads and helps prevent corrosion.[9]

Mud corrosion—Drilling mud also plays a key role in corrosion prevention. In addition to its well-known functions, mud must also remain noncorrosive. A greater awareness of corrosion problems has come about by the lower pH of polymer muds. Low pH means more acidic and hence more corrosive. Oil-base muds are usually noncorrosive and, before the introduction of polymer muds, water-base muds were used with relatively high pH of 10 or greater. So when polymer muds were introduced, corrosion from mud became more apparent.

Dissolved gases are the primary cause of corrosion in drilling fluids. The most common are oxygen, carbon dioxide and hydrogen sulfide. Oxygen, even in concentrations as low as 1 part per million (ppm), is capable of causing serious damage (*top*).

Oxygen can enter the mud system at many points, especially at the surface mixing and storage tanks, and at the shaker screens. Other entry points are at the centrifugal pumps, desanders and desilters. As a result, the mud is usually oxygen-saturated before it reaches the mud pumps. Sodium sulfite- or ammonium bisulfite-based oxygen scavengers, such as Dowell's IDSCAV, are routinely used in mud systems. These chemicals bond with oxygen in the mud to reduce its corrosivity.

Maintaining high pH is important in controlling corrosion rates by neutralizing acids caused by H_2S or CO_2. Hydrogen sulfide can enter the mud system directly from the formation or from thermally degraded mud products, SRBs or makeup water (*above, right*). Scavengers, such as sodium chromate, zinc chromate, and sodium nitrite, can quickly remove H_2S. Dowell's film-forming inhibitors IDFILM, help protect the drillstring and casing. Triazine compounds are used in products such as Dowell's IDCIDE as biocides to control bacteria.[10]
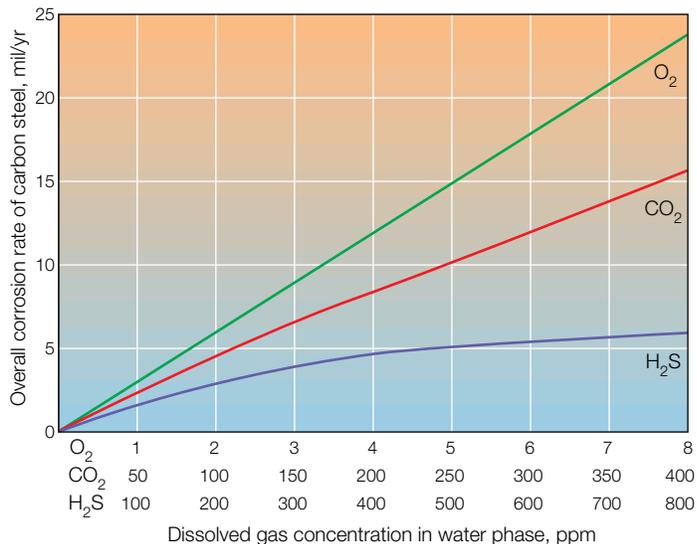
□*Comparison of corrosion rates of steel. Measurements of the corrosion rates of a carbon steel exposed to different concentrations of O_2, CO_2 and H_2S gases dissolved in water, show that O_2 is about 80 times more corrosive than CO_2 and 400 times more corrosive than H_2S.*
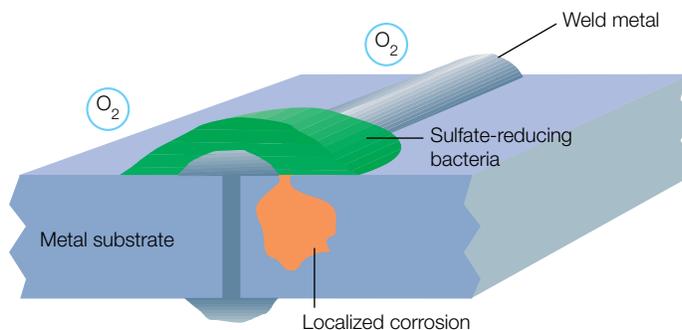
□*Localized bacterial corrosion. Colonies of sulfate-reducing bacteria (SRB) form a deposit under which crevice corrosion develops. The SRBs introduce H_2S into the system, which causes the corrosion.*

9. *ASM Handbook,* reference 1: 1258-1259.
   Jones, reference 1: 61-63.

10. Triazine compounds are derived from carbon, hydrogen and nitrogen compounds based on $C_3H_3N_3$ rings.

11. Bazzari JA: "Well Casing Leaks History and Corrosion Monitoring Study, Wafra Field," paper SPE 17930, presented at the SPE Middle East Oil Technical Conference and Exhibition, Manama, Bahrain, March 11-14, 1989.
   Harari ZY: "Monitoring Short-Term Corrosion Rates in Some Oilwell Cements," *Journal of Petroleum Technology* 42, no. 4 (April 1990): 418-421, 479.

Hydrogen sulfide will induce sulfide stress cracking (see "Corrosion Mechanisms," *page 8*), so any mechanical measures to reduce stress such as decreasing torque or weight-on-bit will limit this type of failure. Surprisingly, high temperature reduces sulfide stress cracking. So if H_2S is detected, it is better to take advantage of high downhole temperatures and treat the mud with the drillstring in the hole.

Corrosion control of CO_2 is similar to H_2S control in that pH must be raised to reduce the acid effects, and drillpipe should be coated with inhibitors. Carbon dioxide can enter the mud system several ways—directly from the formation, by thermal degradation of organic materials, as carbonates from barite or bentonite, chemical over-treatment with soda ash, or bicarbonate of soda. Calcium hydroxide can be used to precipitate carbonates to reduce CO_2 levels.

Completion—After casing has been put in a well, it is usually cemented in place. Cement itself provides primary external protection against corrosion, especially near the surface where circulating aquifer water supplies unlimited oxygen. As a recent study on casing leaks in the Wafra field in Kuwait discovered, the type of cement used is also important. Severe corrosion occurred in wells where construction and permeable light cement were used instead of the usual Portland class G cement with additives.[11] Leakage rates were higher in shallow zones where high sulfate concentrations caused the construction cement—which is nonsulfate resistant—to break down, exposing the exterior of the casing to corrosive aquifer water.

Completion design also plays an important role in preventing internal corrosion. Reducing sand production by gravel pack-

ing prevents sand blasting that causes erosion corrosion. Erosion corrosion will be more pronounced on equipment that restricts flow such as nipples, valves or sharp pipe bends. Once erosion has removed protective coatings, other forms of corrosion can start. The velocity of produced fluids has the same effect as produced sand with erosion occurring at places of turbulence and cavitation.
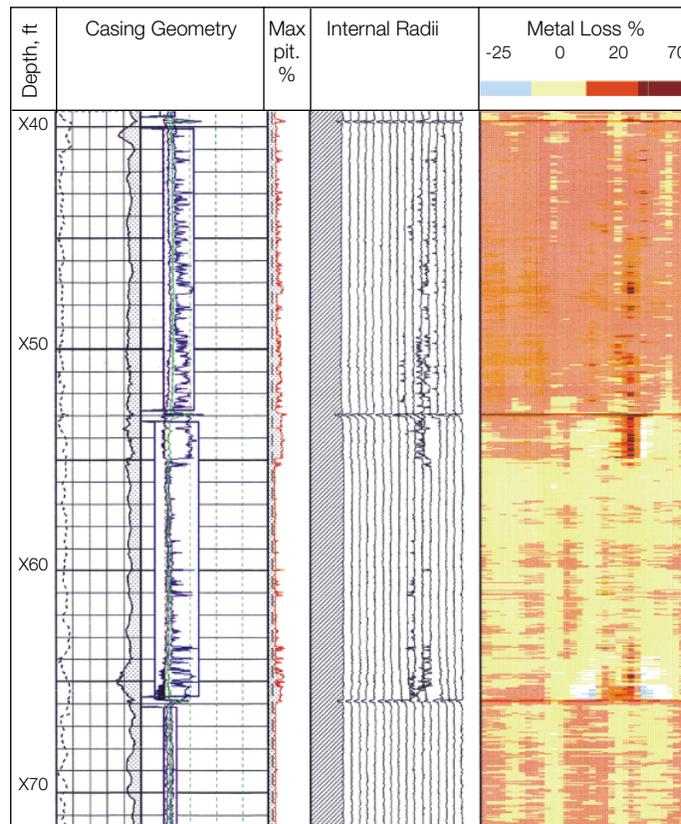
Stimulation programs may, inadvertently, promote internal corrosion. Depending on lithology, highly corrosive hydrochloric acid [HCl] with additions of hydrofluoric [HF] acid are used to improve near-wellbore permeability. These acids can also remove scale buildup on the inside of casing and tubing, allowing direct attack on bare metal. (Scale, produced by iron sulfide and iron carbonate deposits, restricts the corrosion process. Other types of scale are porous and do not protect.) It is therefore essential to use inhibitors and to flow the well to remove spent acid and allow pH levels to increase.

Inhibitors are mixed with acid to provide a protective film over exposed completion strings.[12] The first generation of acid inhibitors was based on highly poisonous arsenic products, but over the years less toxic and more environmentally appropriate products have been developed. The CORBAN range of inhibitors produced by Dowell are designed for acid inhibition of most oilfield tubulars, including coiled tubing, duplex steels and other exotic alloys at up to 400 °F [200 °C].

The type and amount of inhibitor used—inhibitor loading—depends not only on the acid and its strength, but also on the metal it is protecting, the working temperature range and the protection time desired. Inhibitor loadings are determined by measuring the corrosion of samples of casing or tubing—coupons—in a corrosion-test autoclave that duplicates the well-treating environment.

Corrosion during production—Corrosion can continue inside the casing and along completion strings and pipelines during the life of a well. Gas condensate wells may produce gas, hydrocarbons, formation water, acid gases (CO_2 and H_2S) and organic

12. Frenier WW, Hill DG and Jansinski RJ: "Corrosion Inhibitors for Acid Jobs," *Oilfield Review* 1, no. 2 (July 1989): 15-21.

Crowe C, Masmonteil J, Thomas R and Touboul E: "Trends in Matrix Acidizing," *Oilfield Review* 4, no. 4 (October 1992): 24-40.

Samant AK, Koshel KC and Virmani SS, "Azoles as Corrosion Inhibitors for Mild Steel in a Hydrochloric Acid Medium," paper SPE 19022, 1988.

Corrosion Logging Tools

◻MultiFinger Caliper log from the North Sea. This log shows the 16 calipers from the Tubing Geometry Sonde multifinger caliper (middle track). An image of metal loss (right-hand track) shows severe corrosion at X54 ft.

Caliper Devices

Mechanical multifinger calipers have been used for many years to measure the internal diameter of tubing and casing. The Tubing Geometry Sonde (TGS) tool has interchangeable 16-finger sections covering tubing sizes from 2 7/8 to 7 in. [7 to 18 cm]. The larger MultiFinger Caliper (MFC) tool has interchangeable sections with 36, 60 and 72 arms covering casing sizes from 7 to 13 3/8 in. [18 to 34 cm]. Both tools can be run in any borehole fluid and are able to measure small holes as long as a caliper passes over them. Log presentations vary and may be quite sophisticated (above).
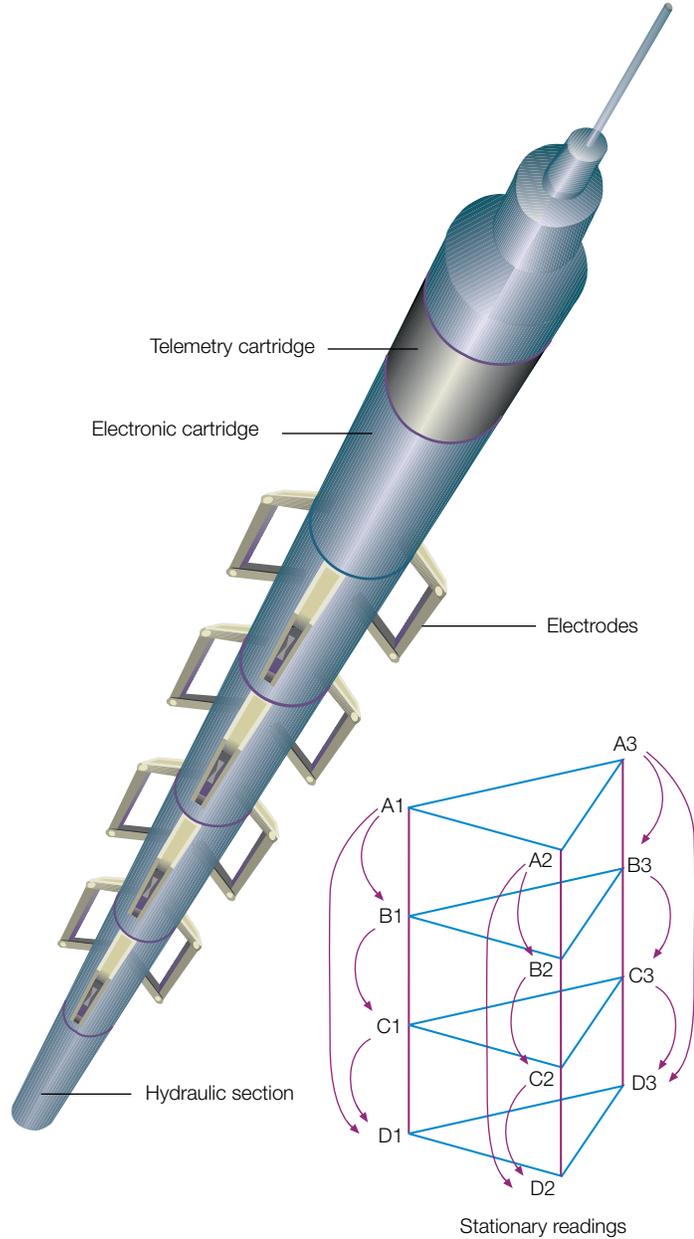
Corrosion Rate Devices

The CPET Corrosion and Protection Evaluation Tool has four sets of three electrodes, spaced at 2-ft [60-cm] intervals along the tool (next page). The tool takes stationary measurements of potential differences and casing resistance between electrode pairs. Casing current is calculated from these measurements at each depth. By taking the difference in current between stations, the radial current density can be calculated and the corrosion rate computed. Casing thickness can also be derived by assuming casing conductivity and using the nominal casing outside diameter. A plot of casing current flow against depth, shows anodic regions where corrosion is likely to occur. If the well is cathodically protected, the log will also show the efficiency of the protection. The tool can be run successively after adjustment of the cathodic protection system current to ensure that anodes have been biased out.

Telemetry cartridge

Electronic cartridge

Electrodes

A3

A1

A2

B3

B1

B2

C3

C1

C2

D3

D1

D2

Stationary readings

Hydraulic section

☐CPET Corrosion and Protection Evaluation Tool. The CPET tool has four sets of three electrodes, each one at the end of a hydraulically operated arm. Stationary readings (inset) are taken and 12 separate contact resistances and electrode potential differences are measured.

Electromagnetic Devices

The METT Multifrequency Electromagnetic Thickness Tool is used to detect large-scale corrosion. It works on the same principle as an induction tool, having a transmitter coil and a receiver coil. The transmitter generates an alternating magnetic field that induces eddy currents in the casing. These produce a secondary magnetic field that interferes with the primary field causing a phase shift. This is detected by the receiver coil. The phase shift is proportional to the total amount of metal surrounding the tool and hence the thickness of the casing. By using a multifrequency transmitter, other properties of the casing that also affect the phase shift can be measured so that thickness can be calculated. An internal caliper measurement is derived from a high-frequency field that penetrates the casing skin only. The casing inside diameter (ID) measurement is not affected by nonmagnetic scale deposits. Monitoring a well over several years using the METT tool gives the general corrosion rate.
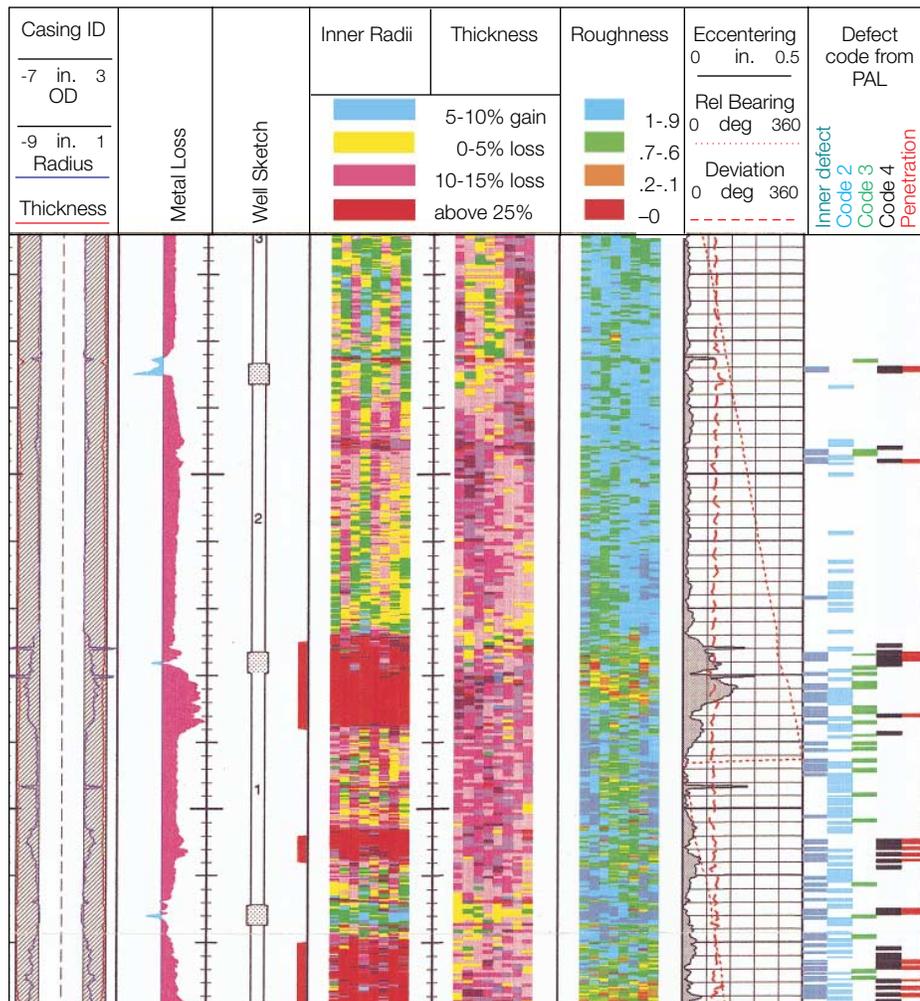
The PAL Pipe Analysis Log tool measures magnetic flux leakage anomalies on the casing wall. Low-frequency magnetic flux is generated by an electromagnet, and pad-mounted sensors detect the anomalies. Inner wall defects are detected by inducing surface eddy currents using a separate coil array with a high-frequency signal. This helps to distinguish internal from external defects. The PAL tool is primarily used to detect casing holes.

The FACT Flux Array Corrosion Tool works on the same principle as the PAL tool, but has a more powerful electromagnet and is designed to negotiate bends down to three times the pipe diameter (3D bends).

Ultrasonic Devices

The USI UltraSonic Imager tool and the CET Cement Evaluation Tool use ultrasonic sound pulses that reflect off and resonate within the casing wall. The transit time of the first received echo gives the internal casing radius. Frequency analysis of the resonant portion of the signal provides casing thickness, allowing internal and external metal loss to be computed. The CET tool has eight transducers equally spaced in a helix around the tool to give a limited casing coverage. The more advanced USI tool has a single rotating transducer to provide full coverage. The

Composite corrosion log legend (track headers):

Casing ID		Inner Radii	Thickness	Roughness	Eccentering	Defect code from PAL
-7 in. 3 OD					0 in. 0.5	
-9 in. 1 Radius	Metal Loss	Well Sketch	5-10% gain (blue)	1-.9 (blue)	Rel Bearing 0 deg 360	Inner defect (Code 2)
Thickness			0-5% loss (yellow)	.7-.6 (green)	Deviation 0 deg 360	Code 3 / Code 4 / Penetration
			10-15% loss (pink)	.2-.1 (orange)		
			above 25% (red)	–0 (red)		

Composite corrosion log. Three corrosion tools have provided the data for this composite log. Track 1 shows the nominal casing ID and OD along with the ID and OD from the CET Cement Evaluation Tool and indicates the presence of corrosion, or scale or wax buildup. Track 2 shows the total metal loss from the METT Multifrequency Electromagnetic Thickness Tool. Track 3 shows the well sketch along with a flag if the corrosion is more than 50%. Track 4 shows the increase or decrease in radius images generated from the eight transducers of the CET tool. Track 5 shows the increase or decrease in casing thickness from the CET tool. Track 6 shows roughness image, again from the CET tool, to indicate the presence of pitting or scale. Track 7 gives casing geometry information from the CET tool. Track 8 gives defect identification from the PAL Pipe Analysis Log tool. The coding has been accepted by the National Association of Corrosion Engineers (NACE) and the Energy Resources Conservation Board (ERCB) in Canada. Code 2 means 20 to 40% of wall penetration; code 3, 40 to 60% wall penetration; code 4, 60 to 80% wall penetration; inner defect means over 20% wall penetration and penetration means a potential hole.

CET and USI tools were developed to record cement bond and inspect the casing.

The Borehole Televiewer (BHTV) tool, Acoustic TeleScanner (ATS) and the UBI Ultrasonic Borehole Imager tool were all developed for openhole applications and employ a rotating transducer. The ATS and UBI tools use a focused transducer to show much finer detail than the CET or USI tools.

All acoustic tools are affected by dense highly attenuating muds and casing scale. They also, at present, do not work in gas-filled holes.

Composite Logs

Many corrosion tools can be combined to give a detailed picture of internal or external corrosion, general corrosion or pits and holes. Modern computers can present these data in many different ways according to customer requirements (above).

acids.[13] Wells that produce formation water, or allow it to condense, are likely to corrode; this may occur anywhere in the tubing string, wellhead or flowline. Higher temperatures accelerate the corrosion rate, as does faster flow. Corrosion increases with water salinity up to about 5% of sodium chloride. Above this, the solubility of oxygen in the water decreases reducing corrosion rates. In fact, when the salt content is above 15%, the rates are lower than with fresh water (*next page, top*). When water and acid gases are present, the corrosion rates rise rapidly. Water dissolves CO_2 or H_2S and becomes acidic.

In highly corrosive environments, carbon steel can be protected by corrosion inhibitors during production.[14] Like acid corrosion inhibitors, these adhere to casing and completion strings to form a protective film. Inhibitors can be continuously introduced into a producing well by a capillary tube run on the outside of the tubing as part of the completion design (*next page, right*). Other methods include batch treatment where inhibitor is pumped down the tubing regularly, say every six weeks, or squeeze treatments, where inhibitor is pumped into the formation.

To protect wells and pipelines from external corrosion, cathodic protection is used.[15] In remote areas sacrificial ground beds may be used for both wells and pipelines (*next page, left*). A single ground bed can protect up to 50 miles [80 km] of pipeline. In the Middle East, solar panels have been used to power impressed current cathodic protection systems. Other methods include thermoelectric generators fueled directly from the pipeline. To protect several wells, a central generator may be used and a distribu-

13. Gunaltun Y: "Carbon Dioxide Corrosion in Oil Wells," paper SPE 21330, presented at the SPE Middle East Oil Show, Manama, Bahrain, November 16-19, 1991.

    Crolet J-L and Bonis MR: "Prediction of the Risks of CO_2 Corrosion in Oil and Gas Wells," paper SPE 20835, presented at the Offshore Technology Conference, Houston, Texas, USA, May 7-10, 1990.

14. Argent CJ, Kokoszka CL, Dale MJ and Hindmarsh MW: "A Total System Approach to Sweet Gas Corrosion Control by Inhibition," paper SPE 23153, presented at the Offshore Europe Conference, Aberdeen, Scotland, September 3-6, 1991.

    Stephens RM and Mohamed MF: "Corrosion Monitoring and Inhibition in Khuff Gas Wells," paper SPE 11511, presented at the SPE Middle East Oil Technology Conference, Manama, Bahrain, March 14-17, 1983.

15. Seubert MK: "Design Parameters for Offshore Well Casing Cathodic Protection," paper SPE 17934, presented at the SPE Middle East Oil Technical Conference and Exhibition, Manama, Bahrain, March 11-14, 1989.
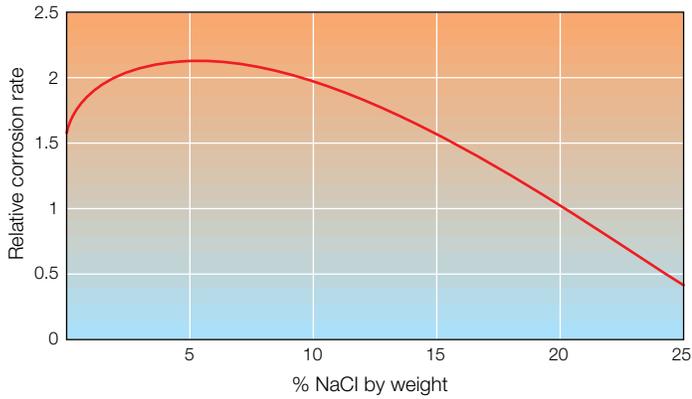
■ *Corrosive effects of sodium chloride [NaCl]. As the weight percentage of NaCl increases up to about 5%, the corrosion rate increases rapidly. Increasing the salt content above this reduces the solubility of oxygen, so the corrosion rate decreases and at about 15% NaCl, the rate is less than with fresh water.*
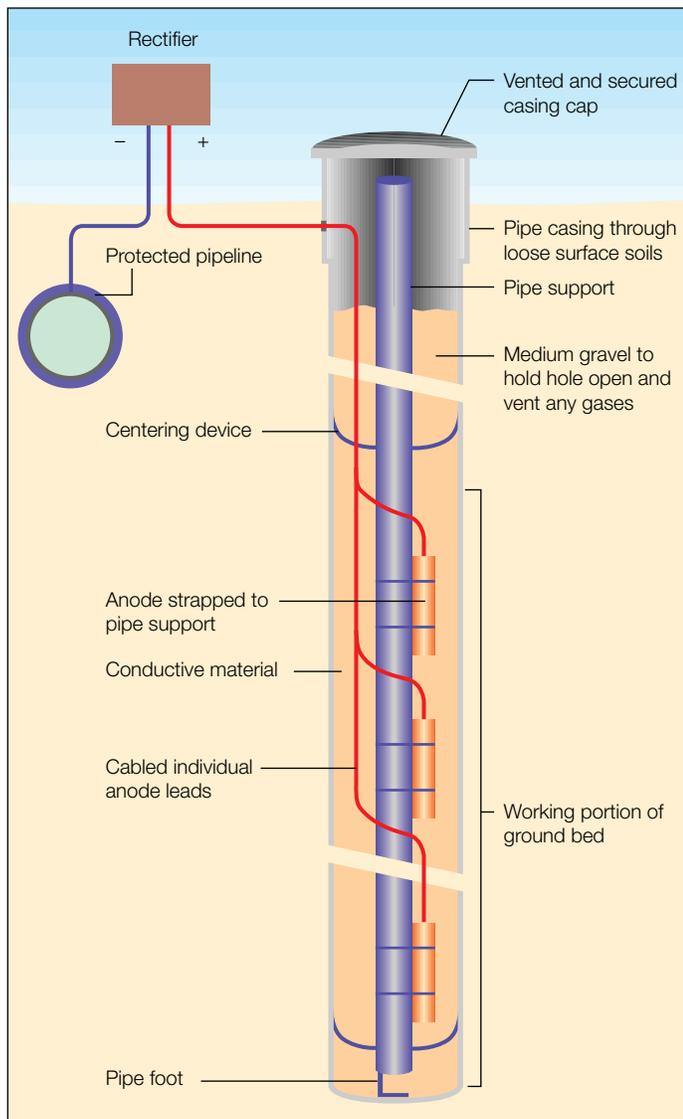
■ *Typical cathodic protection installation for a pipeline. Sacrificial anodes are buried deep underground in a hole filled with conductive material to ensure electrical continuity between the anodes through the ground to the pipeline. The circuit is completed by connecting a cable through a rectifier to the pipeline. The rectifier ensures that the cathodic protection system does not reverse, causing the pipeline to corrode.*
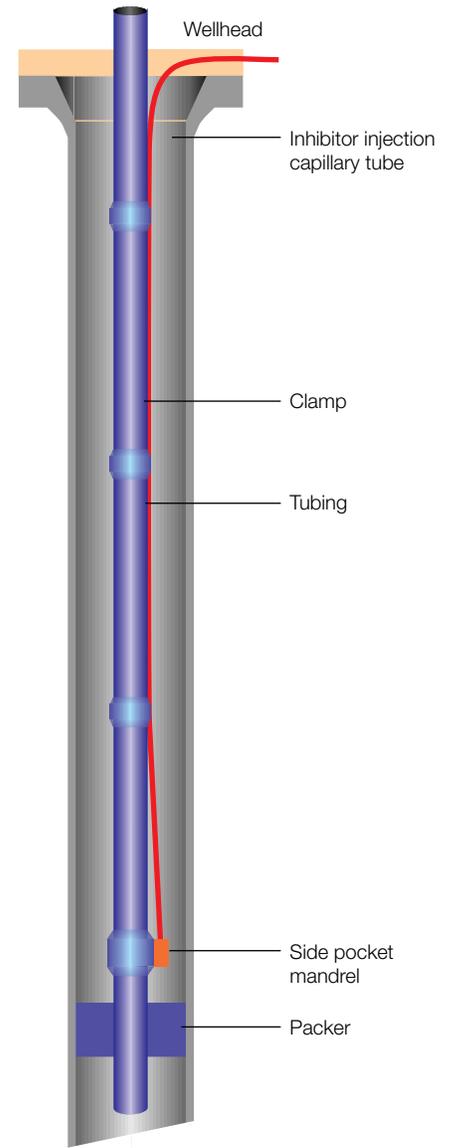
■ *Capillary tube inhibitor injection. Inhibitors are chemicals that are absorbed onto a metal surface from solution to protect against corrosion. The protective film slows corrosion by increasing anodic and cathodic polarization, reducing diffusion of ions to the metal surface, increasing the electrical resistance at the metal-electrolyte interface and by increasing the hydrogen over voltage—the voltage required to remove hydrogen and prevent a buildup stifling the corrosion process. The choice of inhibitor depends on the metal to be protected and its environment. Equally important is the method of application. Shown is a continuous injection method to protect tubing. Inhibitor is pumped down a capillary tube strapped to the outside of the tubing to a side pocket mandrel where it will then mix with production fluid and form a protective film on the inside.*

Steel ring   Plastic Insulator

Drillpipe

Tool joint
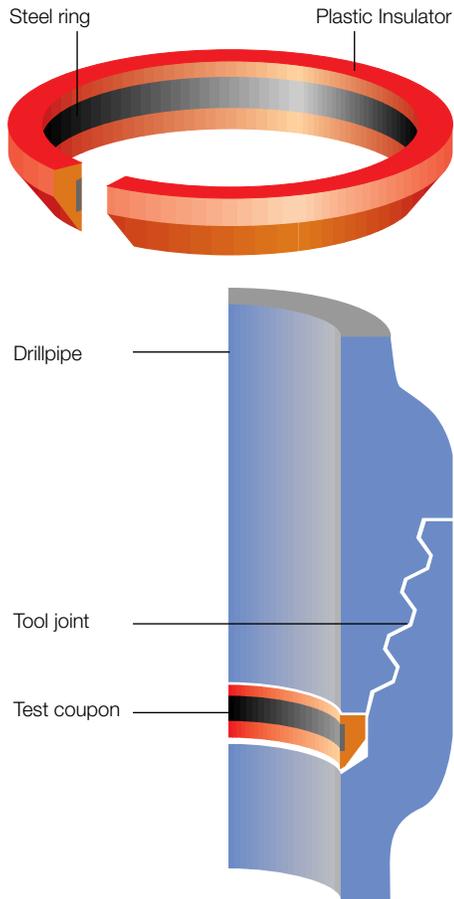
Test coupon

Test coupon for monitoring corrosion of drillpipe. Test coupons may be inserted in any type of pipe work to monitor corrosion. Rings inserted in the tool joints of drillpipe are later removed and examined to monitor corrosion type and corrosion rate—the assumption being that the coupons corrode at the same rate as the drillpipe. Mud engineers also use drillpipe coupons to check the corrosive properties of the mud system.

tion network set up. Wells should be insulated from pipelines so that protection systems do not cause unwanted anodic regions and stray current corrosion.

Under the right conditions, iron sulfide and iron carbonate scales—the corrosion products when H_2S or CO_2 are present—provide protective coatings. The composition of production fluids, however, may change during the life of a reservoir so relying on natural protection may not be wise. Corrosion monitoring, in some form, should always be undertaken.
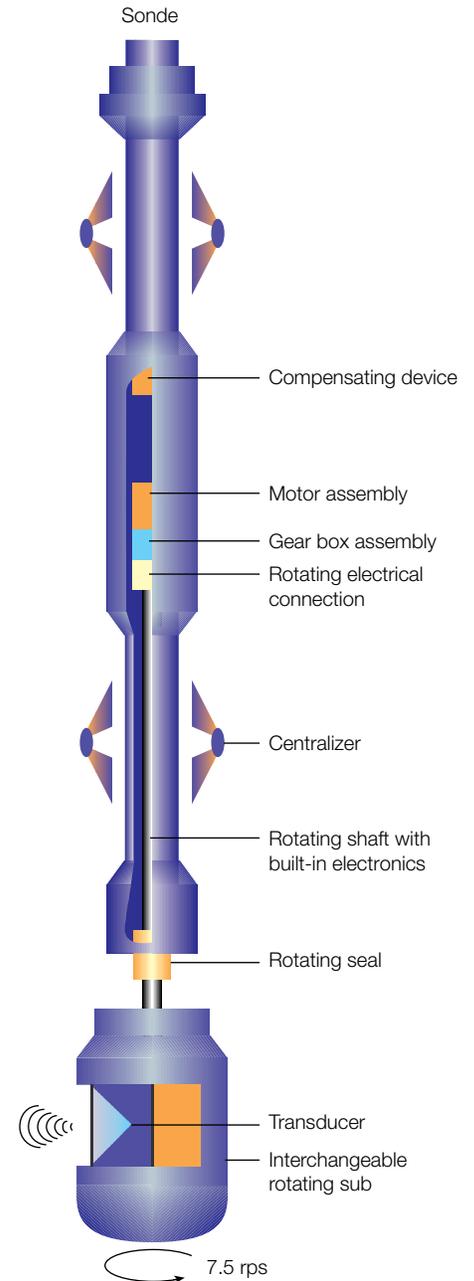
Monitoring Corrosion

Corrosion monitoring is just as important as recognizing the problem and applying controls. Monitoring attempts to assess the useful life of equipment, when corrosion conditions change and how effective the controls are. Techniques used for monitoring depend on what the equipment is, what it is used for and where it is located.

Structures—Monitoring corrosion on exposed structures is fairly straightforward and is carried out by visual inspection. More rigorous tests are required when a structure is load-bearing. Some form of nondestructive testing is used, such as magnetic particle testing to reveal cracks.[16] Sedco Forex rigs are inspected every four years and require underwater divers or remote operated vehicles (ROVs) using still or video photography to check the condition of legs and risers. During this inspection the corrosion rate of sacrificial anodes can be assessed. Normally anodes are designed to last seven or eight years so they will have to be replaced during the typical 20-year life of a rig.

Drillpipe—To monitor drillpipe corrosion and the effectiveness of mud treatments, coupon rings are installed between joints (*left*). The rate of corrosion can then be assessed by measuring the amount of metal lost from the rings. Rates of 0.5 to 2 lbm/ft²/yr [2.4 to 9.8 kg/m²/yr] without pitting are acceptable. Drillpipe is also regularly inspected on racks by ultrasonic and X-ray techniques.

Mud—During drilling, mud systems are routinely monitored for chemical and physical properties. Tests specifically related to corrosion control include an analysis of oxygen, CO_2, H_2S and bacteria. Hydrogen sulfide is detected by measuring the total

Sonde

Compensating device

Motor assembly

Gear box assembly

Rotating electrical connection

Centralizer

Rotating shaft with built-in electronics

Rotating seal

Transducer

Interchangeable rotating sub

7.5 rps

The UBI Ultrasonic Borehole Imager tool. The UBI tool uses a rotating focused transducer to produce an image of the casing. The transducer fires an ultrasonic pulse at the casing. Some energy is reflected back to the transducer from the internal surface of the casing. By measuring the time between transducer firing and the arrival of the first echo an accurate casing internal diameter is calculated. The amplitude of the first arrival also gives a vivid image of the inner casing surface. The tool has a vertical resolution of 0.2 in. [5 mm].

level of soluble sulfides. Mud filtrate can be tested further by adding acid to liberate H_2S, which can be measured using any standard H_2S detector such as a Draeger tube. Bacterial attacks can be recognized by a drop in pH, increase in fluid loss or change in viscosity. Anaerobic bacteria can turn the mud black and produce a smell of rotten eggs.

Casing and tubing—Various corrosion logging tools measure internal corrosion, external corrosion and even evaluate cathodic protection of oil wells (see "Corrosion Logging Tools" page 12).[17] One of the most commonly used techniques has been the multifinger caliper run on either slickline or electric line. This measures the internal radius of casing and tubing using lightly sprung feeler arms. (Heavy springing can cause the fingers to leave tracks through protective scales and chemical inhibitors leading to enhanced corrosion from running the survey itself!) An improvement on contact calipers is the ultrasonic caliper (*previous page, right*), which uses a rotating ultrasonic transducer to measure the echo time of a high-frequency sonic pulse. The processed signal produces a map of the casing. A recent development using a specially focused transducer designed for open hole and currently under development for cased hole, shows remarkable cased hole detail (*right*). The perforations are clearly seen.

Wireline logging provides a good evaluation of downhole corrosion, but disrupts production and may involve pulling completions. Oil companies, therefore, like to use surface monitoring methods to indicate when downhole inspection is required.

Pipelines—Surface monitors include test coupons placed at strategic points in the flowline and also more sophisticated techniques that attempt to measure corrosion rates directly (resistance devices, polarization devices, galvanic probes, hydrogen probes and iron counts).[18] This approach to monitoring can be hit or miss when trying to relate surface corrosion to downhole corro-
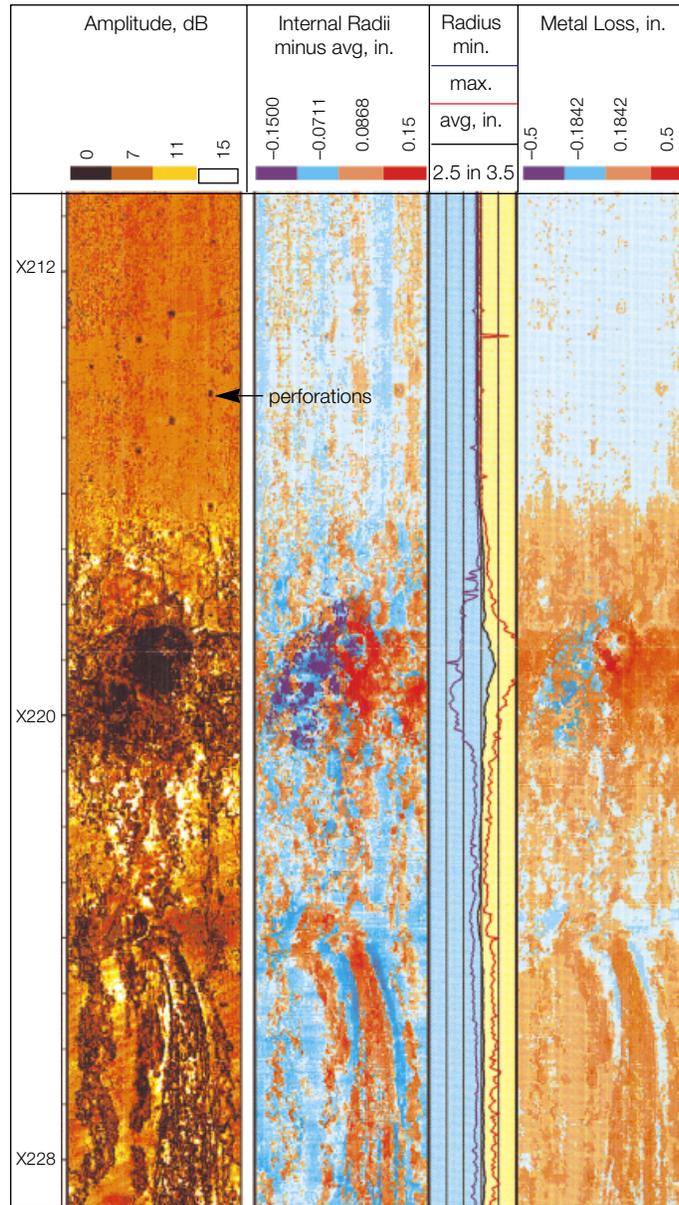
□ *UBI log in cased hole. This log is presented on a scale of 1:10 and shows a large hole in the 7-in. liner around X220 ft. Just above the corroded hole is a pattern of several smaller holes where the casing has been perforated. Track 1 shows the amplitude image, Track 2 the increase or decrease in the internal radius image and Track 4 shows the metal loss image. Track 3 gives a cross section of the well.*

16. Barreau et al, reference 7.

17. Bettis FE, Crane LR, Schwanitz BJ and Cook MR: "Ultrasound Logging in Cased Boreholes Pipe Wear," paper SPE 26318, presented at the 68th SPE Annual Technical Conference and Exhibition, Houston, Texas, USA, October 3-6, 1993.

Kolthof WJ and van der Wal D: "The Use of Digitised Tubing Caliper Data for Workover Planning," paper SPE 23134, presented at the Offshore Europe Conference, Aberdeen, Scotland, September 3-6, 1991.

Cryer J, Dennis B, Lewis R, Palmer K and Watfa M: "Logging Techniques for Casing Corrosion," *The Technical Review* 35, no. 4 (October 1987): 32-39.

Davies DH and Sasaki K: "Advances in Well Casing Cathodic Protection Evaluation," *Materials Performance* 28, no. 8 (August 1989): 17-24.

18. Fincher DR and Nestle AC: "A Review of Corrosion Monitoring Techniques," paper SPE 4220, presented at the Symposium on the Handling of Oilfield Waters of the SPE of AIME, Los Angeles, California, USA, December 4-5, 1972.

Galbraith JM: "In-Service Corrosion Monitoring With Automated Ultrasonic Testing Systems," paper SPE 22097, presented at the International Arctic Technology Conference, Anchorage, Alaska, USA, May 29-31, 1991.

sion. In the past, the onset of well problems instigated monitoring. While waiting for a failure is not recommended, recovering corroded tubing or casing at least provides valuable after-the-fact information, and every opportunity is taken to find out what caused the corrosion and the failure.

Some downhole monitoring techniques have been adapted to logging pipelines.[19] The same surface logging equipment is used, but the logging tools themselves have been made more flexible to pass around sharp bends (*right*). Short lengths of pipe may be logged by this method, but longer lengths are usually monitored by smart pigs. These are sophisticated instrument packages, which use ultrasonic, flux leakage and other electromagnetic techniques to check for corrosion. The data are usually stored in the pig itself for later retrieval. The pig is pumped along a pipeline from a specially-built launching station to a purpose-built receiving section of the pipeline. Surveys cover tens or even hundreds of miles.

Conclusion

The oil industry has invested heavily in material and personnel to try to tame corrosion and prevent metal from returning to its natural state. New oil fields benefit from predevelopment planning and the growing knowledge of all aspects of corrosion control and monitoring. Older fields will continue to benefit from the expertise of the corrosion engineer and the constant monitoring required to prevent disaster. —AM

19. Edwards RC: "Pipeline Corrosion Logging: A New Application of Wireline Surveys," paper SPE 17743, presented at the SPE Gas Technology Symposium, Dallas, Texas, USA, June 13-15, 1988.

Electronics

Pad-mounted sensors and electromagnet
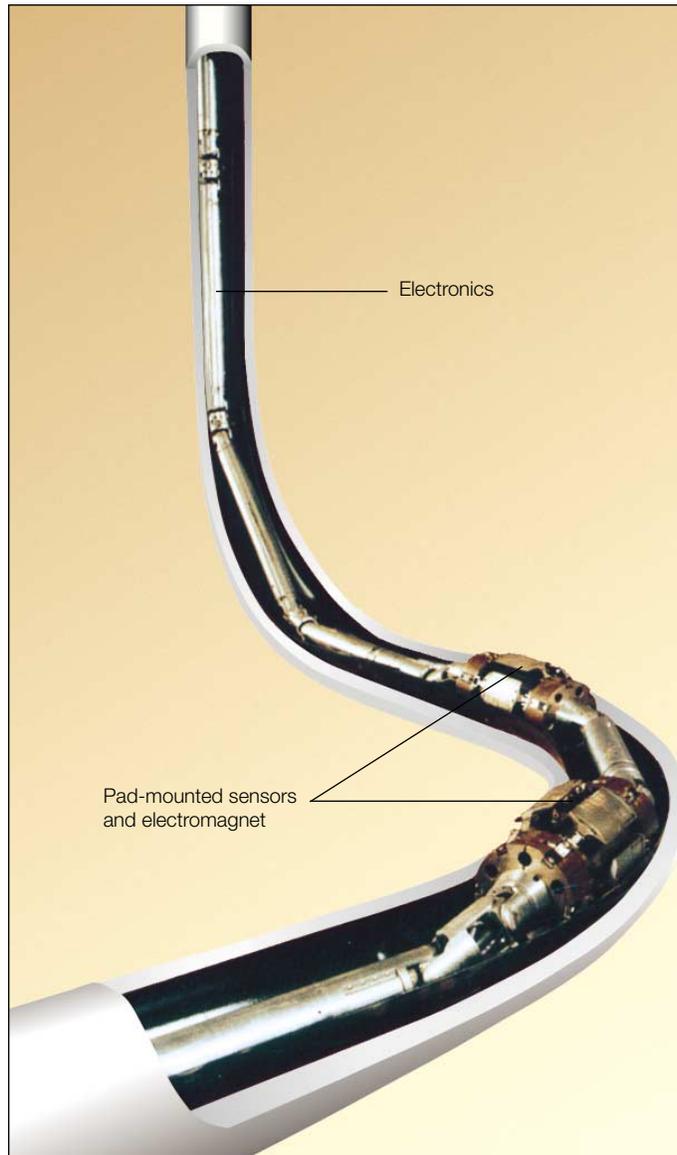
□*The FACT Flux Array Corrosion Tool. This highly articulated sensor measures flux leakage and eddy current anomalies associated with pit or crevice corrosion on pipeline walls. A powerful electromagnet generates low-frequency magnetic flux. Corrosion causes changes in the flux, inducing a voltage in the pad-mounted sensor coils. Separate coils detect inner wall defects by inducing surface eddy currents with a high-frequency signal. This helps distinguish internal from external defects detected by the flux leakage coils.*