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Techniques for Monitoring Corrosion and Related Parameters in Field Applications

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Foreword

Assessment of corrosion in the field is complex due to the wide variety of applications, process conditions, and fluid phases that exist in industrial plants where corrosion occurs. A wide range of direct and indirect measurement techniques is available, but each technique has its strengths and weaknesses. In some applications certain techniques cannot be used at all. Some techniques can be used on-line, while others are done off-line. Commonly more than one technique is used so that the weaknesses of one are compensated for by the strengths of another. In other cases, a combination of different techniques can be synergistic, such as process sampling along with detection of a corrosion upset.

The purpose of this technical committee report is to analyze the various techniques with respect to their benefits and limitations across the wide spectrum of industries in which they are employed. One technique, such as pH measurement, has considerably different features depending on the industry and environment in which it is used. Input to this report has been taken from as wide a spectrum of experienced field users as possible.

This report is intended as a practical reference for both new and experienced users. For new users, it will assist in providing an understanding of the practical aspects of each technique. For experienced users, it will be helpful in assessing less commonly used techniques, or the implications of using a familiar technique in a totally different operating environment.

There are several ways in which the many techniques can be subdivided. Here the categories have been selected on the following basis:

Direct Techniques	—	Intrusive
	—	Nonintrusive
Indirect Techniques	—	On-Line
	—	Off-Line

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Direct techniques are those that measure parameters directly affected by the corrosion process. Indirect techniques are those that provide data on parameters that either affect, or are affected by, the corrosiveness of the environment or the products of the corrosion process. The above categorization provides a good method of segregating the techniques. In general, the techniques have been categorized by their most common usage.

Intrusive techniques are any of those that require access through the pipe or vessel wall in order for measurements to be made. *Intrusive* or *nonintrusive* is not a definition of whether the probe projects into the process flow or not. Most commonly intrusive techniques make use of some form of probe or test specimen, and these techniques include flush probe designs.

It was realized during the preparation of this report that categorizing some techniques as *inspection* rather than *monitoring* was somewhat arbitrary. Monitoring and inspection are essentially descriptions of opposite ends of the measurement spectrum. It is hard to draw an exact dividing line between them based on the sensitivity of the technique, or when the implementation of the technique effectively reduces its sensitivity. The more sensitive monitoring techniques can detect corrosion-related changes as they occur and permit remedial actions to be taken before significant damage occurs. Such techniques are defined as *real-time* measurements. The less sensitive techniques, or inspection techniques, sometimes do not permit remedial measures to be taken before significant damage has occurred.

While this report covers as many techniques as the committee could define, it should also be pointed out that many of these techniques are not widely used in the field for a variety of reasons, involving complexity, cost, suitability for field use, their proprietary nature, field support, technical expertise of the operator, and their applicability to the wide range of plant applications. In general, the most common techniques currently used are mass-loss coupons, electrical resistance probes, linear polarization probes, and ultrasonics.

Some recent developments of differential magnetic flux probes have not yet been validated for field use at the time of this report.

Leak detection techniques have not been included because they are used as failure detection techniques rather than prevention detection techniques. This is not to say they are not useful in their own right, only that they are not within the scope of this report.

This NACE technical committee report was prepared by Task Group T-3T-3, a component of Unit Committee T-3T on On-Line Monitoring Technology. It is issued under the auspices of Group Committee T-3 on Corrosion Science and Technology.

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Section 1: Definition of Terms

Direct Measurement: Describes measurement of metal loss or corrosion rate.

Indirect Measurement: Describes measurement of any parameters that may influence, or are influenced by, metal loss or corrosion.

In-Line Monitoring: Refers to installation of monitoring equipment directly in the bulk fluid of the process, but data acquisition requires extraction of probes or process shutdown for analysis, e.g., mass-loss coupons.

Intrusive Monitoring: Requires penetration through the pipe or vessel wall to gain access to the interior of the equipment.

Nonintrusive Monitoring: Monitoring from the outside of the pipe or vessel wall without having to gain access to the interior of the equipment.

On-Line Monitoring: Refers to installation of monitoring equipment for continuous measurement of metal loss, corrosion rate, or other parameters in an operating system. Data are obtained without the removing the monitoring device.

Off-Line Monitoring: Refers to monitoring methods in which a sample is taken for subsequent analysis.

Real-Time Measurements: Refers to measurements that can detect changes in the parameter under investigation essentially as they occur. The changes can be detected because the technique is sufficiently sensitive, and can be made continuously or with sufficient frequency to follow the changes in the parameter. (This is particularly relevant for many of the measurement techniques that require a significant cycle time.)

Sample: A small quantity of fluid that has been removed from the process stream for testing purposes.

Side (Slip) Stream: A bypass loop or a direct outlet from the process stream. (Fluid may or may not be at the same velocity, temperature, and pressure as the main process stream).

Section 2: Direct Intrusive Measurement Techniques

2.1 Physical Techniques

Definition and Scope

Physical techniques determine metal loss by measuring the change in the geometry of the exposed test specimen. There are many properties of a test specimen that may change to some degree as a result of corrosion, such as its mass, electrical resistance, magnetic flux, reflectivity, moment of inertia, stiffness, or harmonic frequencies. The type of degradation and the physical property change to be studied have been carefully considered in the design of the exposed test specimen. For instance, a test specimen to study cracking usually has a different configuration than a test specimen to study general corrosion or pitting corrosion. When the physical property is measured by electronic means the test specimen can remain in situ and frequent readings are possible. If the test specimen needs to be removed from the process to have its physical property measured, frequent readings are less easy to implement.

The accuracy of these measurements is independent of the electrochemistry of the corrosion processes, or the phase (gas, liquid, or solid) of the environment in which the measurements are made.

Characteristics of the Techniques

(a) Metal loss is measured, and from this measurement the rate of metal loss over time is computed.
(b) These techniques are sensitive to metal loss from erosion and corrosion.
(c) Metal loss techniques are generally more sensitive as the test specimen thickness is reduced or the area is

increased. Direct measurements on actual facility material are less sensitive than on a thin intrusive test specimen.

Benefits

(a) These techniques have a wide application because they can be used in virtually any process environment.
(b) The accuracy of these measurement techniques is independent of the variations in the electrochemistry of the corrosion reactions.
(c) These techniques measure the metal loss due to pure erosion that electrochemical techniques do not measure.

Limitations

Some physical evidence of the corrosion mechanism may be obtained only on inspection of the intrusive device.

2.1.1 Mass-Loss Coupons

Definition and Scope

Mass-loss coupons are small test specimens of metal that are exposed to an environment of interest for a period of time to determine the reaction of the metal to the environment. The mass-loss coupon is removed at the end of the test period and any remaining corrosion products mechanically and/or chemically removed.

The environment of interest can be the full process flow at a location where the conditions are deemed to be suitably severe to give a meaningful representation. Alternatively, the coupon can be exposed in a side stream that can be isolated from the main process stream. It also allows modifying of the flow or temperature of the stream to make the result of the exposure more meaningful. The design of the coupon usually matches the objective of the test—simple flat sheets for general corrosion or pitting, welded coupons for local corrosion in weldments, stressed or precracked test specimens for stress corrosion cracking. Coupons can be complex and consist of metal couples, or incorporate connectors or crevices. The average corrosion rate over that period can be determined from the mass loss of metal over the period of exposure. The technique is an in-line or side-stream monitoring method but does not provide real-time measurements.

Other Sources of Pertinent Information

ASTM(1) G 4 (latest revision). "Standard Guide for Conducting Corrosion Coupon Tests in Field Applications." West Conshohocken, PA: ASTM.

ASTM G 31 (latest revision). "Standard Practice for Laboratory Immersion Corrosion Testing of Metals." West Conshohocken, PA: ASTM.

Freeman, R.A., and D.C. Silverman. "Error Propagation in Coupon Immersion Tests." *Corrosion* 48, 6 (1992): p. 463.

NACE Standard RP0775 (latest revision). "Preparation and Installation of Corrosion Coupons and Interpretation of Test Data in Oil Field Operations." Houston, TX: NACE International.

NACE Standard RP0497 (latest revision). "Field Corrosion Evaluation Using Metallic Test Specimens." Houston, TX: NACE.

Characteristics of the Technique

(a) Mass-loss coupons provide good test specimens for subsequent visual and analytical examination.
(b) Mass-loss coupons allow assessment of pitting, crevice corrosion, and other nonuniform corrosion.
(c) Mass-loss coupon analysis provides additional information over that obtained from electrochemical techniques of corrosion monitoring.
(d) In general, the length of exposure is typically as long as possible to allow for initiation of localized corrosion and adequate evaluation of service conditions. A minimum exposure of three months has normally been used for evaluation of pitting and crevice corrosion. For general corrosion ASTM G 31[1] describes a minimum test duration in hours that is approximately 50 divided by the expected corrosion rate in mm/y (or 2,000 divided by the expected corrosion rate if expressed in mpy). This can vary according to whether the tests are done in well-controlled situations such as laboratory tests or in the field. In the laboratory, where accumulation of corrosion products does not occur, it is possible to obtain good corrosion rate information with much smaller mass-loss quantities. The criteria given by the ASTM standard represents 12 µm (0.50 mil), which is much greater than the detectability limits for mass-loss measurements. Optimum exposure is dependent on the system.
(e) General characteristics of physical techniques are given in Paragraph 2.1.

Benefits

(a) The principle of the technique is easily understood.
(b) Different alloys can be compared easily in a relatively small space.
(c) The mass-loss coupon itself is generally relatively low in cost.
(d) General benefits of physical techniques are given in Paragraph 2.1.

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(1) American Society for Testing and Materials (ASTM), 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.

Limitations

(a) The technique only determines average rate of metal loss over the period of exposure.
(b) Short exposure periods normally yield unrepresentative average rates of metal loss. This is often the result of higher metal loss during initial acclimation to the process environment, which is not typical of the rate after acclimation, or of the plant material.
(c) Determination of the timing or magnitude of corrosion upsets within the exposure period is not possible.
(d) Corrosion rates can only be calculated after mass-loss coupon removal from the system.
(e) Reinsertion of a used coupon is generally not possible.
(f) The procedures for mass-loss coupon cleaning and analysis are labor-intensive, with the consequent additional cost and time required for analysis.
(g) General limitations of physical techniques are given in Paragraph 2.1.

2.1.2 Electrical Resistance (ER)

Definition and Scope

The electrical resistance technique operates on the principle that the electrical resistance of a measuring element (wire, strip, or tube of metal) increases as its conductive cross-sectional area decreases as the result of corrosion, erosion, or a combination of both. In practice, the electrical resistance ratio between a measuring element exposed to the test environment and a reference element protected from the environment is made to compensate for resistance changes due to temperature. Because the resistance of the measurement element is very small, very sensitive measurement electronics are used. The general assumption that the cross-sectional area of the measurement element reduces uniformly as metal loss occurs is made in this method. The technique is an on-line, or side-stream, method that provides real-time measurements when sufficiently sensitive probes are used.

Other Sources of Pertinent Information

ASTM G 96 (latest revision). "Standard Guide for On-Line Monitoring of Corrosion in Plant Equipment (Electrical and Electrochemical Methods)." West Conshohocken, PA: ASTM.

NACE Publication 3D170 (latest revision). "Electrical and Electrochemical Methods for Determining Corrosion Rates." Houston, TX: NACE.

Characteristics of the Technique

(a) Measurement resolution is typically 1 part in 1,000 of the total measuring range of the probe, and the probe range is typically from 0.05 to 0.64 mm (0.002 to 0.025 in.)
(b) Correct probe sensitivity is needed for adequate resolution of corrosion rate and speed of response to upset conditions.
(c) Measured resistance changes are small so that thermal, stress, or electrical noise can affect the signal, necessitating hardware and software filtering, and can increase the time over which corrosion rate is measured.
(d) Corrosion rates can be determined on a time base of hours to days.
(e) Metal loss is measured from any source: corrosion, erosion, or a combination of both (erosion-corrosion).
(f) If used for erosion measurement, some element types need correction for the ratio of area of metal loss to total element surface area.
(g) Dewpoint corrosion effects can be simulated by cooling a bypass stream in which the probe is mounted, or in some cases by cooling the probe.
(h) General characteristics of physical techniques are given in Paragraph 2.1.

Benefits

(a) This technique enables continuous monitoring, which is important for control of corrosion in process equipment, when knowledge of the rate of attack is needed on an ongoing basis.
(b) This technique can be used in virtually any environment.
(c) Process upsets and other corrosive conditions can be detected quickly to enable remedial action to be taken before significant damage to process equipment occurs.
(d) Measurements are made without the need to withdraw coupons from the system.
(e) The technique is useful in monitoring and determining corrosion inhibitor additions.
(f) This technique is useful for the optimization of a corrosion inhibition program, especially for batch treatment programs. It provides information about the inhibitor film persistence and the treatment frequency.
(g) This technique can be used to estimate metal loss due to erosion, by choice of a relatively corrosion-resistant alloy element that has an element with a similar hardness and roughness.
(h) General benefits of physical techniques are given in Paragraph 2.1.

Limitations

(a) Results are representative for metal loss by general corrosion. Probes are less sensitive to effects of localized attack, which increase the element resistance on only a small area of the element, except near the end of probe life on loop element probes, where the localized attack completely corrodes through the element, increasing its resistance to infinity. Special probes can be prepared for sensitivity to crevice

corrosion by creating multiple crevices on the measurement element, such as beads on wire loop probes.
(b) Corrosion rate determination requires a longer time (normally a few hours to a few days) than for electrochemical techniques, for those environments in which electrochemical techniques can be used.
(c) In some situations, partially conductive deposits such as iron sulfide reduce apparent corrosion rates or show some apparent metal gain. Some element shapes are much less sensitive to this than others.
(d) Although the measurements are corrected for temperature change by having a reference element, there can still be small changes in the reading with temperature swings because the measurement element may respond more quickly than the reference element. If these wide temperature swings exist, it can be difficult to separate changes in corrosion rate from changes due to temperature, especially in short-cycle batch operations.
(e) General limitations of physical techniques are given in Paragraph 2.1.

2.1.3 Visual Inspection

Definition and Scope

Visual inspection and measurement of corrosion damage is desirable, but most frequently not possible without a system shutdown. The primary purpose of most monitoring techniques is to make measurements without a shutdown. However, in some instances it may be possible to use visual techniques without shutting down the system, such as in water systems at moderate temperatures, by using boroscopes or video cameras. In a shutdown condition, access to vessels can be sufficient to make direct measurements of localized pitting depths with micrometers. In less accessible areas such as tubes, a calibrated boroscope can be used to make similar pit depth measurements.

Other Sources of Pertinent Information

ASME Boiler & Pressure Vessel Code, Section V (latest revision). “Nondestructive Examination.” New York, NY: ASME.

ASME Boiler & Pressure Vessel Code, Section VIII, Division 1 (latest revision). “Rules for Construction of Pressure Vessels.” New York, NY: ASME.

ASNT(2) Recommended Practice No. SNT-TC-1A (latest revision). “Personnel Qualification and Certification in Nondestructive Testing.” Columbus, OH: ASNT.

Characteristics of the Technique

(a) When physical access to the corroded area is available, pit depth micrometers can be used.
(b) When access is restricted, boroscopes that can measure pit depth by calibrated focusing can be used.
(c) Video cameras can be used in areas with restricted space, for general assessment of visual conditions but without physical measurements.

Benefits

(a) Large areas can be quickly scanned and localized areas of corrosion or corrosion damage can be identified quickly.
(b) Actual pit depths can be measured and pitting rates calculated.
(c) Video cameras and boroscopes can be used in conditions, such as radioactive environments, that are not suitable for personnel.

Limitations

(a) Generally cannot be performed unless the system is shut down.
(b) Boroscopes and video cameras can only be used to make measurements with the system in operation if the process fluid is sufficiently transparent.

2.2 Electrochemical Techniques

Electrochemical techniques, in general, measure the propensity of the metal ions of an alloy to pass into solution (i.e., corrode), by measurement of potentials and current density on a corroding electrode system introduced into the process fluid to be monitored. The metal of the actual plant equipment is not normally part of the measurement circuit. Potentials, current density, or both of these, that result from naturally occurring or externally imposed conditions can be measured, according to the specific electrochemical technique. These characteristics of the current-potential relationship allow assessments of, for example, corrosion rate or pitting propensity. Conversions of the measurements into corrosion rate or other meaningful data use equations or algorithms that are specific to the technique that is used. In those techniques in which corrosion rates are being determined, the conversion of the measured current density into a corrosion rate is governed by Faraday’s Law, empirically determined constants for the system (called Tafel slopes), and other factors in the equation. The determination of the value of these factors is based on knowledge of the following: valency of the corrosion reactions; assumptions about the relative corrosion rates of the elements that make up the alloy; and assumptions of the relative noninterference of reactions other than the primary corrosion reactions (see ASTM Standards G 96[2] and G 102[3]). For electrochemical measurements in any

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(2) American Society for Nondestructive Testing (ASNT), 1711 Arlingate, Columbus, OH 43228-0518.

quantitative form, the electrodes are fully submerged and in conductive contact with a sufficiently conductive environment, normally water. Fluid conductivity is important with all of these techniques and is equipment-specific. Several variations of measurement techniques are used on the electrochemical interface of an alloy with its conductive ionic media. Some techniques use analysis of the interface with direct current (DC) methods. Other techniques, or extensions of the DC techniques, use alternating current (AC) methods to provide further characterization of the corrosion interface and the conductivity of the process fluid.

Limits of operation for field use vary from those applicable for the same techniques in the laboratory, mostly for reasons of practical probe geometry. For example, capillary salt bridges to reference electrodes help reduce the interference of solution resistance in laboratory measurements, but these can be too delicate for field use. When a reference electrode is used, it normally is sufficiently stable relative to the measurements that are to be made. Correlation with metal loss on the measurement electrodes can significantly improve reliability and accuracy of corrosion rate calculations by compensating for unknowns in the exact form of the corrosion reactions.

Characteristics of the Technique

(a) The measurements can perturb the natural electrochemical mechanisms of corrosion that are to be measured.
(b) The techniques use a continuous and sufficiently conductive process fluid that is often, but not always, a single-phase liquid flow.
(c) In multiphase conditions or dewpoint/condensation conditions, the electrodes are positioned in such a way that the conductive phase completely covers the electrodes and interconnects the electrodes for quantitative measurements.
(d) In multiphase systems with low water content, monitoring in stagnant liquid collection points is not always representative of corrosion rates in the process stream. Special designs can be used to obtain a continuous and representative condition of the passing water phase.
(e) The location, installation, and positioning of probes is critical. Oil fouling and deposits can impede the successful operation of the probe.
(f) Depending on the type of measurement technique, an appropriate reference electrode that is compatible with the process is typically used and is recorded with the data.

Benefits

(a) These techniques can generally give faster and more dynamic information related to corrosion rate changes than other techniques.
(b) More mechanistic information on the corrosion process stream can be obtained from electrochemical techniques.
(c) Some derivations of electrochemical techniques address the degree of localized corrosion.

Limitations

(a) In multiphase systems, nonconductive phases can temporarily isolate the electrodes and invalidate the readings until the electrodes are clear again, or they can permanently isolate the electrodes until they are removed and cleaned.
(b) Corrosion rate measurements based on the underlying theory assume uniform corrosion. Localized corrosion can be detected but not measured.
(c) The specific electrode reactions and polarization coefficients (ß) may be unknown. In this case estimates are used for the conversion of polarization resistance into a corrosion rate.
(d) Other secondary reactions at or near the corrosion surface can interfere with the measurement and produce an erroneous corrosion rate.
(e) Deposits on electrodes can affect the results.
(f) Bridging of electrodes with conductive deposits causes short circuits that affect results and can render them invalid until the electrodes are cleaned.
(g) Metal loss by pure erosion is not measured. However, erosion may remove corrosion products exposing the base material, which can then corrode faster (erosion-corrosion).

2.2.1 DC Techniques

2.2.1.1 Linear Polarization Resistance (LPR)

Definition and Scope

The basic technique of LPR determines the corrosion rate of an electrode. The propensity of the metal ions of the electrode (cations) to pass into solution, or corrode, is inferred from the ratio between a small change in applied potential (typically 10 to 20 mV) around the open-circuit potential of the electrode and the corresponding change in the current density. The electrode is normally polarized both cathodically and anodically by reversal of the impressed current and held at the polarized potential until a stable current density can be measured. The ratio of the change of potential to the change of current density ($\Delta E/\Delta I_{app}$) relates to corrosion rate through the Stern Geary equation:

$$\Delta E/\Delta I_{app} = ß_a ß_c / (2.3\ i_{corr}\ (ß_a + ß_c)$$

Where:

$ß_a$ = the estimated or measured Tafel slope for the anodic reaction
$ß_c$ = the estimated or measured Tafel slope for the cathodic reaction
ΔE = the applied potential change
Δi_{app} = the resultant current density change
i_{corr} = the corrosion current density at the free-corroding potential

The corrosion current density is related to corrosion rate by Faraday's Law.

LPR probes are typically a two- or three-electrode configuration with either flush or projecting electrodes.

With a three-electrode system, the corrosion measurement is made on the test electrode. Because the measurement takes only a few minutes, a stable reference electrode is not necessary; the potential of a half electrode is normally sufficiently stable. The reference electrode typically is stainless steel or even the same alloy as that being monitored on the test electrode. The auxiliary electrode is normally also of the alloy being monitored. The proximity of the reference electrode to the test electrode governs the degree to which compensation for solution resistance is effective.

With a two-electrode system, the corrosion measurement is an average of the rate for both electrodes. Both electrodes are of the alloy being monitored.

A combination of an LPR and a zero resistance ammeter (ZRA) measurement has been used by some investigators to measure the rate of localized corrosion, such as pitting, crevice, or underdeposit corrosion in aqueous solutions. In this method, a large-area electrode is placed in fast flow conditions, and two small electrodes are placed in slow flow conditions. A side-stream differential flow cell is normally used for this purpose. The large area electrode and each of the small electrodes are connected together with a ZRA. The large electrode becomes a cathode, and the small electrodes become anodes, due to differential aeration. Consequently, the small anodes experience preferential corrosion. As immersion time increases, the anodes become covered with deposits. From then on the corrosion attack on the anodes is quite uniform, so that the average corrosion rate on the anodes represents an underdeposit or localized corrosion rate. The localized corrosion rate for each small electrode is computed as the combination of an LPR measurement between the two small electrodes (with the ZRA disconnected), and a ZRA measurement between the large cathode and each of the small anodes. The solution-corrected LPR measurement between the two small electrodes provides the component of corrosion current on the small electrodes, resulting from their surface condition only. The separate ZRA measurement provides the component of corrosion current that results from the galvanic cell between the large cathode and each of the small anodes. The LPR and ZRA measurements are made separately, because the LPR measurements would be invalid if made while a superimposed galvanic current was applied.

The technique is an on-line, or side-stream, method that provides real-time measurements.

Other Sources of Pertinent Information

ASTM G 59 (latest revision). "Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements." West Conshohocken, PA: ASTM.

ASTM G 96 (latest revision). "Standard Guide for On-Line Monitoring of Corrosion in Plant Equipment (Electrical and Electrochemical Methods)." West Conshohocken, PA: ASTM.

ASTM G 102 (latest revision). "Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements." West Conshohocken, PA: ASTM.

Mansfeld, F. "The Polarization Resistance Techniques for Measuring Corrosion Currents." In *Advances in Corrosion Science and Technology*, vol. 6. Eds. M.G. Fontana and R.W. Staehle. New York, NY: Plenum Press, 1976), pp. 163-262.

NACE Publication 3D170 (latest revision). "Electrical and Electrochemical Methods for Determining Corrosion Rates." Houston, TX: NACE.

Scully, J.R. "The Polarization Resistance Method for Determination of Instantaneous Corrosion Rates: A Review." CORROSION/98, paper no. 304. Houston, TX: NACE, 1998.

Stern, M., and A.L. Geary. "Electrochemical Polarization 1. A Theoretical Analysis of the Shape of Polarization Curves." *Journal of the Electrochemical Society* 104, 1 (1957): p. 56.

Yang, B. "Real Time Localized Corrosion Monitoring in Refinery Cooling Water Systems." CORROSION/98, paper no. 595. Houston, TX: NACE, 1998.

Characteristics of the Technique

(a) An estimate of corrosion rate can be made with a single measurement.
(b) This technique enables corrosion to be monitored on a continuous basis.
(c) A two-electrode probe, or a three-electrode probe with a reference electrode equidistant from the test and auxiliary electrode,

do not compensate for errors due to solution resistance.

(d) A three-electrode probe can reduce the effect of solution resistance (IR drop) depending on its position and proximity to the test electrode.

(e) Some two-electrode probe systems use a high-frequency AC signal to short circuit the double-layer capacitance to measure and correct for solution resistance (IR drop).

(f) Empirically determined conversion constants (Tafel slopes) are generally used for calculation of corrosion rates. Tafel slopes can be determined by other techniques, such as curve fitting of polarization resistance curves (i.e., nonlinear polarization resistance), by potentiodynamic polarization scans (see Paragraph 2.2.1.4), or by harmonic distortion analysis (see Paragraph 2.2.2.2).

(g) The polarization resistance technique is based on uniform corrosion and assumes one anodic and one cathodic reaction far removed from the reversible potential. Any departure from these assumptions can compromise the results (see item [c] above).

(h) General characteristics of electrochemical techniques are given in Paragraph 2.2.

Benefits

(a) The technique provides corrosion rate data directly in a few minutes.

(b) The technique is particularly well suited to water applications so that process upsets or other corrosion conditions can be detected quickly to allow remedial action to be taken almost immediately.

(c) The technique can be used to quickly compare the general corrosion performances of corrosion inhibitors in sufficiently conductive environments.

(d) Usually only the metal electrodes of an LPR probe are replaced, providing greater economy. The mass loss of the used electrodes can be determined, providing a means of verification of the average corrosion rate as measured by LPR.

(e) The electrode configuration allows the combination of this technique with other electrochemical measurements, such as zero-resistance ammeter (ZRA) or electrochemical current noise, to provide an indication of the stability of an inhibitor film and/or initiation of localized corrosion on the surface of the metal.

(f) General benefits of electrochemical techniques are given in Paragraph 2.2.

Limitations

(a) The need for a sufficiently conductive medium precludes the use of this technique for many applications in oil and gas, refinery, chemical, and other low-conductivity applications. Solution resistance compensation can extend the range of application, but still excludes many of these applications.

(b) The specific electrode reactions and polarization coefficients can be unknown. In these cases estimates are used for the conversion of polarization resistance into corrosion rate, but these may be inaccurate. Parallel testing of mass-loss coupons or mass loss on the LPR electrodes can reduce this effect.

(c) The method does not use a calibrated reference electrode to establish a potential level. The reference is the open-circuit potential of one of the electrodes. Relative drift of the open-circuit potentials during the measurement cycle affects the measurement.

(d) Significant localized corrosion may distort the general corrosion rate measured by LPR.

(e) General limitations of electrochemical techniques are given in Paragraph 2.2.

2.2.1.2 Zero-Resistance Ammeter (ZRA) Between Dissimilar Alloy Electrodes—Galvanic

Definition and Scope

Galvanic measurements are made between two electrodes of dissimilar metals or occasionally two electrodes of the same alloy, but in a different metallurgical/electrochemical state (see also Paragraph 2.2.1.3—Zero-Resistance Ammeter Between the Same Alloy Electrodes). The electrodes under test are immersed in the ionic (i.e., electrically conductive) media. The differences in the electrochemical behavior of the two electrodes in the process stream give rise to differences in the redox potential of the two electrodes. Once the two electrodes are externally electrically connected, the more noble electrode becomes predominantly cathodic, while the more active electrode becomes predominantly anodic and sacrificial. When the anodic reaction is relatively stable the galvanic current monitors the response of the cathodic reaction to the process stream conditions. When the cathodic reaction is stable, it monitors the response of the anodic reaction to process fluctuations. The ZRA can record small currents between the dissimilar electrodes. The galvanic technique can be used to study directly the corrosion effect on dissimilar alloys in a process stream, or the same alloy in different galvanic state as the result of different heat treatments such as welding, stress relieving, or annealing.

For example, this technique has been used to monitor depolarization effects of the cathode of a galvanic pair of electrodes to obtain feedback of low levels of dissolved gases, particularly oxygen, or the presence of bacteria, which depolarize the cathode of the galvanic pair and increase the coupling current. When used for detection of low levels of oxygen, other dissolved gases can be an interference, and calibration against a dissolved oxygen meter is initially obtained if quantitative values are needed. (See also Paragraph 4.3.3—Dissolved Oxygen.)

A zero-resistance ammeter measures the short-circuit current between the electrodes, by an ammeter with zero resistance, in order to avoid reducing the short-circuit current. In reality, this is done electronically by measuring the current necessary to bring the electrodes to the same potential. However, there is still resistance in the total measurement circuit due to the resistance of the process medium between the electrodes. The technique is an on-line, or side-stream, method that provides real-time measurements.

Other Sources of Pertinent Information

ASTM G 71 (latest revision). "Standard Guide for Conducting and Evaluating Galvanic Corrosion Tests in Electrolytes." West Conshohocken, PA: ASTM.

ASTM G 82 (latest revision). "Standard Guide for Development and Use of a Galvanic Series for Predicting Galvanic Corrosion Performance." West Conshohocken, PA: ASTM.

NACE Publication 1C187 (latest revision). "Use of Galvanic Probe Corrosion Monitors in Oil and Gas Drilling and Production Operations." Houston, TX: NACE.

Characteristics of the Technique

(a) This technique measures the galvanic current between closely coupled dissimilar alloys. As a monitoring tool, this technique shows the response of the galvanic couple to changes in the electrode reactions due to changes in the chemical environment and to changes in the electrical conductivity of the process environment.
(b) Solution conductivity affects the galvanic current between the electrodes even if the external measurement circuit has effectively zero resistance (zero-resistance ammeter).
(c) The ZRA method can be a quantitative method if the number of influencing factors is limited and preferably verifiable through other means. For monitoring dissolved gases, the conversion of the signal to a gas concentration level is not accurate. When other factors play a role as well, for example, in the presence of filming compounds and inhibitors, the method cannot be applied in a quantitative sense.
(d) General characteristics of electrochemical techniques are given in Paragraph 2.2.

Benefits

(a) This technique provides a simple measurement of the activity of single corrosion factors. A nonexhaustive list includes the effectiveness of inhibitors, the effectiveness of alloy-specific inhibitors (e.g., passivators or copper inhibitors), the presence of specific depassivators (e.g., O_2, NH_3, HCN), film forming, and passivation/depassivation, velocity-induced corrosion, and the presence of alloy-specific chelants.
(b) This technique involves a simple in-line device without diaphragms and solutions that can give an indication of dissolved gases, primarily dissolved oxygen, at levels of 0 to 50 ppb. This is the typical range of operation for deaerated systems to control corrosion to acceptable levels.
(c) This technique can be used directly in systems up to approximately 40 MPa (6,000 psi), and it does not need a pressure-reduced side stream that may not be typical of a high-pressure process stream.
(d) General benefits of electrochemical techniques are given in Paragraph 2.2.

Limitations

(a) Results from galvanic probes do not always reflect actual galvanic corrosion rates, because the overall galvanic corrosion rate depends on the relative areas and geometries. These relative areas can vary between the probe and the plant.
(b) High IR drop gives erroneous low results if the electrodes are too far apart relative to the distance between the dissimilar metals in the process stream.
(c) Correlation between measured signals and levels of dissolved oxygen are approximate, and excessive oxygen levels and flow rate variations can affect calibration.
(d) The method cannot distinguish between activation of the anodic or cathodic reaction. For example, an increase in the measured current can result from cathodic activation by increased dissolved oxygen, from anodic activation by increased bacterial activity, or by a combination of these. Separate analysis is sometimes performed if it is necessary to distinguish between them.
(e) General limitations of electrochemical techniques are given in Paragraph 2.2.

2.2.1.3 Zero-Resistance Ammeter (ZRA) Between the Same Alloy Electrodes

Definition and Scope

Zero-resistance ammeter (ZRA) measurements are used on electrodes of nominally the same alloy in electrical current noise techniques (see Paragraph 2.2.1.5), some additions to linear polarization resistance (see Paragraph 2.2.1.1), and in some developmental techniques to investigate biomass.

In the developmental technique used to investigate biomass, one of the nominally identical electrodes is cathodically polarized, which has been shown to encourage bacterial growth on the cathode of the pair. After removal of the polarization, the zero-resistance ammeter measures the current to achieve a certain polarization and the subsequent residual generated current between the electrodes. The change in current can provide an indication of biofilm activity. The measurements are normally made on stainless steel electrodes (relatively noncorrosive) in a carbon steel plant application. The technique is an on-line, or side-stream, method that provides real-time measurements.

Other Sources of Pertinent Information

Licina, G.J., and G. Nekoksa. "An Electrochemical Method for On-Line Monitoring of Biofilm Activity." CORROSION/93, paper no. 403. Houston, TX: NACE, 1993.

Characteristics of the Technique

(a) This technique measures the galvanic current between two connected electrodes of the same alloy.
(b) Solution conductivity affects the galvanic current between the electrodes even if the external measurement circuit has effectively zero resistance (zero-resistance ammeter).
(c) This technique measures the electrical current that flows between two electrodes due to the effect of differences or imbalances between the electrodes that exist or are induced by their previous treatment.
(d) General characteristics of electrochemical techniques are given in Paragraph 2.2.

Benefits

(a) As a form of electrochemical current noise sampling, this technique is useful as an indication of instability due to inhibitor film breakdown and as a qualitative indication of pitting tendency.
(b) When the nominally noncorroding electrodes have been cathodically polarized, microbiological activity is sometimes increased so that an increased current is detected. This can be useful in detecting the presence of microbiological activity in the system.
(c) General benefits of electrochemical techniques are given in Paragraph 2.2.

Limitations

(a) As a pitting tendency measurement, this technique is only qualitative because it samples only the differences between two theoretically identical electrodes.
(b) The technique as used for biomass detection is still under development and evaluation.
(c) When used for biomass detection, this technique does not distinguish between biomass that accelerates corrosion and that which does not.
(d) When used for biomass detection, the period of cathodic polarization to provide the preferential electrode site is sometimes difficult to estimate.
(e) As a biomass indicator, the measurement is qualitative and not quantitative.
(f) General limitations of the electrochemical techniques are given in Paragraph 2.2.

2.2.1.4 Potentiodynamic/Galvanodynamic Polarization

Definition and Scope

Potentiodynamic or galvanodynamic polarization is a technique for studying the electrochemical characteristics of a metal/solution interface by studying the relationship between externally applied DC polarization current and potentials. Normally the results are graphed as a plot of potential against the log of current density, often known as an Evans or Stern diagram. Potentiodynamic polarization is generally used in water systems. Galvanodynamic polarization is sometimes used in systems containing oil, so that current density is controlled. One of the most common uses of the technique is to determine whether crevice corrosion or pitting is a problem and whether general corrosion can be estimated by another technique. It is also often used to estimate the relative susceptibility of various materials to localized corrosion in the process stream. Ideally, each point on the current/potential graph is made by allowing a polarization time of tens of seconds to several minutes to permit the complete charging of the double-layer capacitance associated with the metal/fluid interface and the electrode surface to oxidize or reduce all of the surface deposits and to polarize to the applied potential. Instead, the applied current or applied potential, whichever is the controlling variable, is changed continuously in an analog form at some preset rate (potentiodynamic or galvanodynamic) or in a digital form of small discrete steps at some preset rate (potential staircase or galvanic staircase). In reality, with computer-controlled equipment, the difference between the analog and digital forms becomes only the actual size of the steps. In either case, the faster the rate of change of applied signal, the greater is the lag of the measured signal behind the true steady-state values desired. The compromise between a practical and reasonable time to complete a scan and the degree of lag from measured to ideal response is a key question with this technique. This is particularly the case in the field where the tested environment is continually changing and cannot usually be controlled as it can in the laboratory.

The result is used to assist in analysis of the mechanistic behavior of the metal/solution interface. The technique is used quite commonly in the laboratory, but it is used only occasionally in the field to validate Tafel slopes for systems on which the basic corrosion rate theory is based. The technique is not normally considered as an on-line or real-time method because the electrodes are normally replaced after one or two test runs, because running the test changes the electrode surfaces.

Other Sources of Pertinent Information

ASTM G 5 (latest revision). "Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements." West Conshohocken, PA: ASTM.

ASTM G 61 (latest revision). "Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys." West Conshohocken, PA: ASTM.

NACE Publication 3D170 (latest revision). "Electrical and Electrochemical Methods for Determining Corrosion Rates." Houston, TX: NACE.

Characteristics of the Technique

(a) The technique allows study of both anodic and cathodic corrosion reactions and processes over a wide range of applied potential or current density.
(b) This is one of the techniques used for determination of Tafel slopes, although curve fitting of the polarization resistance method is generally considered to be better. Tafel slopes are fundamental empirical data that are used by electrochemical techniques for the conversion of the actual measured polarization resistance or corrosion current density into an actual corrosion rate.
(c) Extrapolation of the true Tafel slopes to their intersection can provide a measure of corrosion current density from which corrosion rate can be calculated.
(d) Polarization of the metal well away from the corrosion potential can substantially change the surface so that fresh test specimens sometimes are needed for each scan. (Reuse of electrodes for more than one scan after some restabilization period is the subject of considerable discussion.)
(e) Correction for IR drop due to solution resistance is particularly important with this technique because of the relatively high currents (I) used compared with other electrochemical techniques. Determination of the solution resistance (R) is normally made to compute the error produced by IR drop and assess whether a correction needs to be made. The error is usually small in highly conductive solutions.
(f) General characteristics of electrochemical techniques are given in Paragraph 2.2.

Benefits

(a) This technique allows determination of Tafel slopes and corrosion rates.
(b) This technique is also used for the study of localized corrosion (e.g., pitting) and repassivation characteristics.
(c) This technique provides some information on the effectiveness and persistence of a corrosion inhibitor film by determining the potential at which breakdown commences.
(d) General benefits of electrochemical techniques are given in Paragraph 2.2.

Limitations

(a) This technique takes a few hours to produce a single reading, but results can usually be achieved in 45 to 60 minutes.
(b) For calculation of Tafel slope, this method can use data far removed from the corrosion potential and thus incorporate other mechanisms, which may produce significant errors.
(c) Replacement or reacclimation of electrodes after a test, together with the relatively long test time, mean that the technique does not meet the definition of an on-line or real-time monitoring method.
(d) A higher technical-electrochemical skill level is likely to be necessary to interpret the data than for some of the other techniques.
(e) Compensation for solution resistance is much more critical than for other techniques, which makes field applications more difficult because of practical limitations on probe design of effective, closely spaced reference electrodes.
(f) An operator is generally present when this technique is used, and it is used primarily as an investigative tool.

(g) Quantitative pitting rates are not calculated unless a ratio of pitted area to nonpitted area is assumed.
(h) Pitting rates calculated from this technique are not indicative of pitting rates of the normal unpolarized system. The test specimen is in an unrealistic environment when it is forced to pit so that the numbers produced may have relevance only in relative comparisons.
(i) General limitations of electrochemical techniques are given in Paragraph 2.2.

2.2.1.5 Electrochemical Noise (ECN)

Definition and Scope

The electrochemical noise technique measures naturally occurring fluctuations of potential or current. It also can measure current noise under an applied potential, or measure potential noise under an applied current. Current noise is a measurement of current fluctuations between two nominally identical electrodes. Potential noise is a measurement of the potential fluctuations between one electrode and a reference electrode, or between two nominally identical electrodes. The relationship between the potential and current is the same as for the other techniques because they are acting through the same equivalent circuit. The frequency of these fluctuations is typically below 1 Hz.

It is common to couple nominally identical electrodes through a zero-resistance ammeter (ZRA) and measure the potential of this pair against a reference electrode, or third nominally identical electrode. In this manner both electrochemical potential noise and electrochemical current noise are collected. The ZRA by its operation forces these two electrodes to the same potential. The potential of this pair is then measured against the third reference electrode.

The impedance of the corrosion interface is frequency-dependent due to the capacitive and sometimes inductive characteristics of the interface, and time-dependent from the corrosion process. The relationships between potential and current noise are more complex to analyze quantitatively because the naturally occurring fluctuations do not have controlled frequencies as are applied, for example, in electrochemical impedance spectroscopy (EIS) (see Paragraph 2.2.2.1). For these reasons, much of the laboratory development investigation of the technique centers on frequency analysis.

The technique measures current and potential noise on the corroding electrodes, which are consequences of the uniformity or nonuniformity of the adjacent metal electrodes exposed to a process stream. In some cases the effects of crevice corrosion, pitting corrosion, and stress corrosion cracking have been shown by the change in the potential and/or the current signals generated between the two surfaces.

This technique was first developed more than twenty years ago, but an understanding of the method of analysis is still evolving, partly because the technique has been used to look at several types of corrosion. It has generally been used in the field in conjunction with other techniques, largely for comparison purposes. There are still varying conclusions about the accuracy and effectiveness of the technique in its own right. For determination of corrosion rate, it generally follows the trend of other electrochemical methods but sometimes with less accuracy. For determination of pitting and cracking, some successful applications have been reported. In other instances results have been variable because the characteristics are not always repeatable, and cracking and pitting may not be present on the tested specimen. Laboratory analysis and study of the technique are currently under way. It is not a fully evaluated technique for laboratory or field use. The technique is an on-line, or side-stream, method that provides real-time measurements.

Other Sources of Pertinent Information

ASTM STP 1277. "Electrochemical Noise Measurement for Corrosion Applications." Eds. J.R. Kearns and J.R. Scully. West Conshohocken, PA: ASTM.

Eden, D.A., K. Hladky, and D.G. John. "Electrochemical Noise — Simultaneous Monitoring of Potential and Current Noise Signals from Corroding Electrodes." CORROSION/86, paper no. 274. Houston, TX: NACE, 1986.

Rothwell, A.N., T.G. Walsh, and W.M. Cox. "On-Line Corrosion Investigation and Surveillance — Chemical Plant Case Studies." CORROSION/91, paper no. 170. Houston, TX: NACE, 1991.

Characteristics of the Technique

(a) For a transition from passive to pitting initiation, the potential and current noise levels tend to increase. However, if pits begin to propagate, the current noise levels tend to increase, with a decrease in potential noise.
(b) *Noise resistance* (R_n), similar to *polarization resistance* (R_p), can be generated for general corrosion rate. If the signals are analyzed digitally, this is calculated as the ratio of the standard deviation of the potential to the standard deviation

of the current, or on a particular bandwidth as the ratio of the root mean square (rms) of the potential noise divided by the rms of current noise. Some users refer to a localization or pitting index, which is defined as the standard deviation of current noise divided by the rms of current noise.
(c) For calculation of corrosion rates, the analysis is similar to the other electrochemical methods of LPR and EIS.
(d) As corrosion becomes more unstable and nonuniform corrosion or cracking occurs, analysis is much more complex and a qualitative assessment of the corrosion mechanism sometimes is all that is possible.
(e) General characteristics of electrochemical techniques are given in Paragraph 2.2.

Benefits

(a) The effects of nonuniformity from pitting, stress corrosion cracking, and crevice corrosion can often be seen with this technique.
(b) General benefits of electrochemical techniques are given in Paragraph 2.2.

Limitations

(a) Although the effects of pitting, crevice corrosion, and cracking can often be seen in the measurements, algorithms to convert the measured signals to definitive outputs are mostly empirical, nondisclosed, and are developed for specific applications.
(b) The form of quantitative analysis for these nonuniform corrosion mechanisms is a subject of research and discussion. Therefore, in field applications it is generally considered suitable for qualitative purposes only.
(c) Correlation with general corrosion rates from other electrochemical techniques and metal-loss methods tends to vary, suggesting that the technique is still not fully understood.
(d) The recommendations for use of the technique for on-line monitoring currently vary considerably. However, there seem to be a growing number of users who have had increasing success with the technique.
(e) There is currently no agreed standard guide or reference method to test and calibrate ECN instrumentation, such as ASTM G 54 for potentiodynamic measurements (UNS(3) 43000 in H_2SO_4). Until such tests or dummy cells are agreed on, it is difficult to know whether the equipment is working properly.
(f) General limitations of electrochemical techniques are given in Paragraph 2.2.

2.2.2 AC Techniques

2.2.2.1 Electrochemical Impedance Spectroscopy (EIS)

Definition and Scope

Electrochemical impedance spectroscopy (EIS) is the AC electrochemical measurement technique. The technique measures the electrical response of the metal/solution interface over a range of frequencies, typically 1 mHz to 10 kHz.

Analysis of a frequency scan provides phase-shift information, which is essential to modeling of an equivalent circuit of the electrochemical metal/ solution interface for evaluation of the corrosion mechanism. The high-frequency response is used to determine the component of solution resistance included in the measurement. This is used to remove the effect of solution resistance from the low-frequency measurement from which the polarization resistance can then be determined. To convert the polarization resistance into a corrosion rate involves an empirical measurement of the Tafel slope for the metal/solution interface and the equivalent mass and density of the alloy (see ASTM G 102[3]). Tafel slopes can be determined by other techniques such as potentiodynamic polarization (Paragraph 2.2.1.4) or harmonic distortion analysis (Paragraph 2.2.2.2). The technique is primarily used in controlled laboratory analysis, but is also now being applied in some plant environments in its full-frequency scan form, as well as in a modified form, by the use of one or more selected frequencies.

The measurement cycle time depends on the frequency ranges used, especially the low frequencies. A single frequency cycle at 1 mHz takes 15 minutes. A typical high- to low-frequency scan takes two hours. If the number of different frequency steps is reduced to only four on active metals without a coating, and low frequency is limited to 1 mHz, the measurement cycle time can be reduced to around 40 minutes. Simultaneous application of multiple frequencies can reduce this time but increases the complexity of the electronics. The technique is not generally used as on-line or real-time monitoring in the field but is used primarily in the laboratory. However, in principle it is capable of being an on-line or real-time monitor.

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(3) Metals and Alloys in the Unified Numbering System (latest revision), a joint publication of the American Society for Testing and Materials (ASTM) and the Society of Automotive Engineers Inc. (SAE), 400 Commonwealth Dr., Warrendale, PA 15096.

Other Sources of Pertinent Information

ASTM STP 1188. "Electrochemical Impedance: Analysis and Interpretation." Eds. J.R. Scully, D.C. Silverman, and M.W. Kendig. West Conshohocken, PA: ASTM.

Rothwell, A.N., T.G. Walsh, and W.M. Cox. "On-Line Corrosion Investigation and Surveillance-Chemical Plant Case Studies." CORROSION/91, paper no. 170. Houston, TX: NACE, 1991.

Silverman, D.C. "Primer on the AC Impedance Technique." In *Electrochemical Techniques for Corrosion Engineering*. Ed. R. Baboian. Houston, TX: NACE, 1986, p. 73.

Silverman, D.C. "Technical Note: On Ambiguities in Modeling Electrochemical Impedance Spectra Using Circuit Analogues." *Corrosion* 47, 2 (1991): p. 87.

Characteristics of the Technique

(a) The technique applies AC potentials or voltage perturbations instead of DC potentials or voltage perturbations to the corrosion interface, and these signals are normally within 10 mV of the corrosion potential.
(b) The need for use of multiple frequencies for measurement increases the time used for a test. The number of frequencies used can be varied to reduce the time of a test depending on the resolution required for the test. Multiple frequencies can also be applied simultaneously, but this makes analysis more complex and comparatively less accurate.
(c) A change in the shape of the impedance response over time can be related to corrosion rate changes or inhibitor film breakdown.
(d) The measurement uses a steady-state corrosion potential, as does polarization resistance.
(e) High-sensitivity instruments have been successfully used in low-electrical-noise areas and in carefully controlled flow cells with stable chemical conditions such as in a laboratory. In the field, lower sensitivities are obtainable, and simplified aspects of the technique are sometimes used in their own right or as an enhancement to DC techniques.
(f) General characteristics of electrochemical techniques are given in Paragraph 2.2.

Benefits

(a) This AC technique permits better analysis of the electrical characteristics of the corrosion interface than other techniques, if the spectra can be interpreted properly.
(b) The measurement of solution and coating resistance, within the compliance of the instrument, makes the technique useful in lower-conductivity environments and in the investigation of degradation of coatings and linings.
(c) General benefits of electrochemical techniques are given in Paragraph 2.2.

Limitations

(a) Complex analysis is sometimes performed to obtain information.
(b) Circuit analogs can be ambiguous.
(c) A higher technical level of understanding is generally considered necessary to use this technique than other techniques.
(d) This technique is inappropriate for use to investigate localized corrosion because the technique provides an average measurement for the entire exposure surface.
(e) This technique cannot be used with wide temperature and composition swings.
(f) This technique is limited primarily to laboratory studies.
(g) General limitations of electrochemical techniques are given in Paragraph 2.2.

2.2.2.2 Harmonic Distortion Analysis

Definition and Scope

Harmonic distortion analysis is a relatively new form of electrochemical analysis and still unproven in most areas of its proposed use, not only in the laboratory but also in the field. It has also been called harmonic impedance spectroscopy, although this is misleading because impedance is not computed. With this technique, a low-frequency sinusoidal potential is applied to a three-electrode measurement system, and the resulting current is measured. If the relationship between applied potential and the measured current in a DC sense were perfectly linear, then on application of a sinusoidal potential, only a current of the same frequency would be measured with no harmonics of the applied potential frequency. However, because the relationship in reality is not linear, this causes harmonics of the fundamental applied frequency to be produced in the current measurement. These harmonic frequency responses are the basis of harmonic distortion analysis.

In principle, analyzing the primary frequency and the harmonics makes it possible to extract all the information to calculate Tafel slopes and corrosion rate. The practice has been used in a very limited number of applications to date with some reasonable success. The speed with which the Tafel slopes can be determined is a particular attraction of the technique.

The technique has been used to estimate corrosion rates at potentials well away from the corrosion potential, such as on cathodically protected structures. This method, however, is considered by some to have no theoretical basis, and in practice it has not produced corrosion rates that agree with independent measurements. The technique is capable of being used on-line to provide real-time measurements.

Other Sources of Pertinent Information

Meszaros, L., G. Meszaros, and D. Lengyel. "Application of Harmonic Analysis in the Measuring Technique of Corrosion." *Journal of Electrochemical Society* 141, 8 (1994): p. 2068.

Characteristics of the Technique

(a) The technique applies a single, low-frequency and low-distortion, sinusoidal voltage to the corrosion interface. As a quality check, three different frequencies are used to verify the repeatability of the technique. The amplitude is in the region of 10 to 30 mV peak to peak.
(b) The frequency used is typically 0.1 to 10 Hz. Other frequencies can be used depending on the corrosion process.
(c) The theoretical analysis for the computation of Tafel slopes and corrosion current makes no assumptions about solution resistance effects.
(d) The sinusoidal measurement is made at the corrosion potential
(e) Measurements cannot be performed unless the system is free of significant electrical noise in the frequency range of the applied measurement potential, or one of its harmonic frequencies. Correct filtering is critical, but noise rejection can be excellent.
(f) This technique uses a three-electrode system.
(g) The effect of double-layer capacitance is generally compensated.
(h) General characteristics of electrochemical techniques are given in Paragraph 2.2.

Benefits

(a) The theory derives expressions of the harmonic content to compute directly the corrosion current at the corrosion potential.
(b) The theory derives expressions for the anodic and cathodic Tafel slopes.
(c) The technique allows a much faster computation (typically less than one minute) for Tafel slopes than from the DC polarization technique.
(d) General benefits of electrochemical techniques are given in Paragraph 2.2.

Limitations

(a) This technique has only been used in a few applications to date.
(b) The general applicability of the technique is still to be demonstrated.
(b) The analysis is more complex and less easily understood than EIS.
(c) Corrosion rate estimates under cathodically or otherwise polarized conditions are doubtful.
(d) Measurements of metal loss under marginal or poor cathodic protection potentials can be monitored more simply with mass-loss coupons or electrical resistance probes.
(e) Correct filtering is critical to any frequency analysis technique.
(f) There are instrumental limitations because with the use of the third harmonic (third derivative), one decimal place tends to be lost with each harmonic or derivative.
(g) General limitations of electrochemical techniques are given in Paragraph 2.2.

Section 3: Direct Nonintrusive Measurement Techniques

By definition direct nonintrusive measurement techniques do not require access to the inside of the pipe or vessel and so avoid any risks associated with on-line insertion and retrieval operations of intrusive devices. These techniques have the advantage of monitoring the actual plant material rather than a possibly slightly different test specimen, and can include often-critical locations such as welds, pipe bends, tees, and similar nonuniformities. Depending on the specific technique and implementation, the area of the plant material monitored is generally larger than on an inserted specimen. With those techniques in which large areas can be scanned, such as magnetic flux, eddy current, or nonfixed ultrasonics, the sensitivity is the lowest, so that a trade-off of sensitivity versus area occurs. In general, measurement techniques that make measurements directly on the plant do not have as high a resolution as do intrusive techniques on test specimens. The consequence of the lower sensitivity of these techniques produces a longer response time to corrosion changes and the probability of missing a short upset altogether.

3.1 Physical Techniques for Metal Loss

3.1.1 Ultrasonics

Definition and Scope

Ultrasonic inspection has been used for decades to measure the thickness of solid objects. A piezoelectric crystal referred to as a transducer is made to oscillate at high frequencies, coupled directly or indirectly to one surface of the object whose thickness is to be measured, and the time a wave of known velocity takes to travel through the material is used to determine its thickness. Since the late 1970s, ultrasonic equipment has been enhanced greatly by combining the basic electronics with computers. However, many of the measurements made are still single-point thickness measurements, which do not provide the capability of the more sophisticated systems. Rugged systems based on modern microcomputers are now available from many sources. These systems, complete with motor-driven robotic devices to manipulate the transducer(s), have created the ability to measure wall thickness of corroded components at tens of thousands of points over 0.1 m^2 (1 ft^2). This capability, coupled with increased precision of field measurements possible with computer-controlled systems, has made these automated ultrasonic systems well suited for on-line corrosion monitoring.

With the more sophisticated systems, in which great numbers of thickness measurements are possible over small areas, statistical comparisons of the areas scanned can allow rapid comparison of selected spots used in a corrosion-monitoring program. The volume of material in the area scanned can be calculated, and this information can then be used to develop volumetric changes over time (or mass loss). The change in area of corrosion can be compared, as can the remaining wall thickness and pit depth, which can be used to calculate pitting rates.

The uses of ultrasonics as described above are primarily considered as inspection, because they are usually concerned with vessel integrity, although in severe cases of metal loss, measurements can be made sufficiently regularly to become more of an ongoing corrosion monitor. Developments are now being made with individual transducers or transducer arrays that are left in place to provide continuous monitoring. Permanently attached transducers improve accuracy by removing errors in relocating a transducer to exactly the same point with exactly the same couplant thickness, depending on the accuracy of the transducer, its temperature compensation, and the measurement frequency. The technique is capable of being used on-line, but its sensitivity generally excludes its use for real-time measurements.

Other Sources of Pertinent Information

ASME(4) Boiler & Pressure Vessel Code, Section V (latest revision). "Nondestructive Examination." New York, NY: ASME.

ASME Boiler & Pressure Vessel Code, Section VIII, Division 1 (latest revision). "Rules for Construction of Pressure Vessels." New York, NY: ASME.

ASNT Recommended Practice No. SNT-TC-1A (latest revision). "Personnel Qualification and Certification in Nondestructive Testing." Columbus, OH: ASNT.

Characteristics of the Technique

(a) Access to one surface of the component is generally necessary.
(b) The accuracy of controlled ultrasonic inspection can approach and exceed ±0.025 mm (±0.001 in. or ±1 mil) in a laboratory setting with proper transducer selection and equipment setup and controlled temperature conditions. Field inspections are typically to within ±0.1 mm (±0.004 in. or ±4 mils); the computer-based systems have made more precise thickness readings possible by controlling the equipment setup, by employing more stable solid-state systems, and by achieving more consistent transducer manipulation than can be accomplished with manual ultrasonic inspection.
(c) Some fixed transducer systems can measure to around ±0.005 mm (±0.0002 in. or ±0.2 mil).
(d) General characteristics of direct nonintrusive measurement techniques are given in the introduction to Section 3.

Benefits

(a) Corrosion-monitoring data can be produced without installation of any device on or in the component being monitored.
(b) Because corroded areas of the actual component are being measured directly, analytical techniques can then be used to determine the integrity of the damaged item. For example, the method published in ANSI(5)/ASME B31G[5] can be used to calculate the maximum allowable operating pressure of piping systems. Similar techniques for calculating the integrity of corroded storage tanks and pressure vessels are available in API(6) Standards 653[6] and 510,[7] respectively.

Limitations

(a) Accuracy of the corrosion-monitoring data and sensitivity to small changes of metal loss is not as high as with physical techniques for metal loss or with electrochemical techniques.
(b) Higher accuracy for monitoring purposes is limited by variations of sound velocity in different metals, by temperature variations in the substrate, and discrimination of the acoustic reflections.
(c) This technique is normally used for corrosion prediction over longer periods of time and is not suited for monitoring real-time corrosion rate changes.

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(4) American Society of Mechanical Engineers (ASME), 345 E. 47th St., New York, NY 10017-2392.
(5) American National Standards Institute (ANSI), 11 W. 42nd St., New York, NY 10036.
(6) American Petroleum Institute (API), 1220 L St. NW, Washington, DC 20005.

3.1.2 Magnetic Flux Leakage (MFL)

Definition and Scope

The magnetic flux leakage (MFL) technique uses a combination of permanent magnets and sensor coils to identify corrosion in steel tube pipe and plate. Magnetic flux is channeled into the component being inspected as the flux makes a circuit between the opposite poles of two magnets. If there is an anomaly in the metal, some flux leaks out and is detected by the sensors placed near the metal's surface and between the magnets. The sensors measure the amplitude of the leaking flux. The amplitude is compared with results from known anomalies in similar materials after the inspection and the analyst then makes wall-loss predictions. MFL has applications in tanks, heat exchangers, pipelines, and tubular products. Different types of MFL systems are used for these different applications. Some systems, such as in-line pipeline inspection tools, are very sophisticated self-contained systems that gather and store various data remotely. Signal analysis can be real-time or done at a later date, depending on the application and the inspection system. Software for signal analysis is available.

MFL is used to monitor corrosion over long periods of time. Information from ongoing inspections is compiled and corrosion rates are determined. Some inspections can be performed on-line while others, such as tank floor inspections, require that the tank be out of service during the inspection.

Other Sources of Pertinent Information

ASME Boiler & Pressure Vessel Code, Section V (latest revision). "Nondestructive Examination." New York, NY: ASME.

ASME Boiler & Pressure Vessel Code, Section VIII, Division 1 (latest revision). "Rules for Construction of Pressure Vessels." New York, NY: ASME.

ASNT Recommended Practice No. SNT-TC-1A (latest revision). "Personnel Qualification and Certification in Nondestructive Testing." Columbus, OH: ASNT.

Characteristics of the Technique

(a) The part or the inspection tool is moving.
(b) Coils are in close proximity to the area being inspected.
(c) Strong magnets are used to induce magnetic flux into the part being inspected.
(d) General characteristics of direct nonintrusive measurement techniques are given in the introduction to Section 3.

Benefits

(a) MFL is useful for locating defects where volumetric material loss, such as pitting, occurs.
(b) MFL is a relatively fast technique for inspecting equipment with large surface areas such as tanks, or long distances in the case of pipelines.
(c) MFL systems are portable and are taken from project site to project site.

Limitations

(a) Depends on surface cleanliness so that sensors have good contact with the part being inspected.
(b) MFL can be susceptible to random noise if the coils bounce off the surface.
(c) Depends on the relative velocity of the tool and the component being inspected remaining constant through the inspection.
(d) In some applications strong magnets can make moving the sensors difficult.
(e) This technique is not sensitive to gradual wall loss.
(f) The sensitivity is fixed if the magnetic field intensity is fixed. Some systems have a variable magnetic field intensity that sets the degree of sensitivity required.
(g) There are temperature limitations when the technique is used on pigging systems.
(h) Reliability is more critical in pigging operations. Electronics, shoes, and brushes may not survive the environment.
(i) Seamless pipe gives more noise due to ripple in thickness, causing chatter of the heads compared with electrically welded pipe.
(j) Calibration against the actual part is necessary.

3.1.3 Electromagnetic—Eddy Current

Definition and Scope

An eddy current is defined as a circulating electrical current induced in a conductive material by an alternating magnetic field. An eddy current system incorporates the electronic signal generator/processor and a probe containing at least one coil. The signal generator uses an alternating current to induce eddy currents in an electrically conductive material. In turn, the induced eddy currents induce an alternating current in the sensing coils. The fields in the generator and sensor coils are balanced by adjustments of frequency, amplitude, and distance. A change in the balance of the two fields indicates various flaws or material thinning. The size of the flaws and the detection limits are important, so that calibration of the system to cracks, pitting, wall thinning, and material change are made. Calibration standards are given in the ASME Boiler and Pressure Vessel Code, Section VIII,[8] and calibration can be made in addition for specific types of flaws. The technique is commonly used off-line to identify defects in nonmagnetic metals such as heat exchanger tubing. Sophisticated, digitized, multichannel eddy current instruments are used extensively throughout industry. Computer-controlled robotic delivery systems to manipulate probes are used in areas such as manufacturing and nuclear power generation.

Signal analysis can be performed real-time or at a later date. Software for automated signal analysis is available.

Generally, eddy current is thought of as an inspection technique. With repeated surveys of the same area on a frequency determined by the severity of the corrosion, metal loss over time can be determined and long-term corrosion rates calculated. The method can be used on-line but this is not common, and the sensitivity is too low to provide real-time measurements.

Other Sources of Pertinent Information

ASME Boiler & Pressure Vessel Code, Section V (latest revision). "Nondestructive Examination." Article 8, "Eddy Current Examination of Tubular Products." New York, NY: ASME.

Characteristics of the Technique

(a) The distance between inspected material and the probe or coil remains constant.
(b) The probe, or the part, is usually moving.
(c) Field data are compared with data from a calibration standard of similar dimensions and material to the part being inspected.
(d) Depending on the orientation of the defect being measured, an accuracy of ±5% of wall thickness can be obtained.
(e) Slightly magnetic materials such as UNS S41000 (400 series) stainless steels can be examined using a magnetically biased probe. The magnet is used to neutralize the permeability effect on the eddy currents.
(f) General characteristics of direct nonintrusive measurement techniques are given in the introduction to Section 3.

Benefits

(a) Eddy current is sensitive to a large number of defects including pitting, general corrosion/erosion, wear from other parts, dents, bulges, cracks, and metallurgical changes such as plating and dealloying.
(b) The technique is a fast technique for use in tube bundles where external access to tubes is limited.
(c) The equipment is portable. In industrial and aerospace settings the same system is used to examine many different pieces of equipment.

Limitations

(a) The surface finish can affect sensitivity.
(b) Signals can be affected by localized changes in magnetic permeability and temperature.
(c) This technique is not sensitive to defects in magnetic material, unless the defect's surface is on the near side.
(d) The sensitivity to defects decreases with depth into the material.

3.1.4 Electromagnetic — Remote Field Technique (RFT)

Definition and Scope

In this technique, changes in the phase and amplitude of a magnetic field linking an exciter coil and a detector coil through a metal are measured to determine changes in the wall thickness of tube or plate. In general, the wall thickness affects the phase between the excitation and detector signals, and the extent of the defect affects the amplitude. Although magnetic flux can be used to measure changes in thickness of both magnetic and nonmagnetic materials, it is generally used to identify defects in magnetic material for which eddy currents are not effective. Sophisticated multichannel digital instruments are now available to measure magnetic flux. The system is composed of electronics to generate, manipulate, and display the magnetic flux signals, and a probe to introduce the magnetic field into the component being inspected. Originally used to inspect oilfield tubulars for corrosion, it now has applications in small-bore tubes and in plate. Typical applications include inspecting heat exchanger and boiler tubes for corrosion or erosion.

Signal analysis can be performed real-time or at a later date. Signal analysis software is available.

Generally, the remote field method is thought of as an inspection technique. With repeated surveys of the same area on a frequency determined by the severity of the corrosion, metal loss over time can be determined and long-term corrosion rates calculated. The method can be used on-line, but this is not common and the sensitivity is too low to provide real-time measurements.

Other Sources of Pertinent Information

ASME Boiler & Pressure Vessel Code, ASME Section V (latest revision). "Nondestructive Examination." Article 8, "Eddy Current Examination of Tubular Products." New York, NY: ASME.

Characteristics of the Technique

(a) Field data are compared with data from a calibration standard of similar dimensions and material to the component being inspected.

(b) The material being inspected needs no unusual cleaning.
(c) Depending on the characteristics of the defect being measured, accuracy of ±10% can be obtained.
(d) General characteristics of direct nonintrusive measurement techniques are given in the introduction to Section 3.

Benefits

(a) RFT is sensitive to defects such as general wall thinning from corrosion or erosion, large or grouped pits, mid-span collision, etc.
(b) It is a fast technique for use in tube bundles for which external access to tubes is limited.
(c) The equipment is portable. The same system can be used to examine many pieces of equipment.
(d) This technique measures internal or external defects equally.

Limitations

(a) External fins can affect the signals.
(b) Localized changes in magnetic permeability and temperature can affect the signals.
(c) Small defects such as closed cracks are not always detected.

3.1.5 Radiography

Definition and Scope

The thickness of corroded piping and other equipment can be deduced from radiographic images in several ways. One such technique has been reported in the literature and has been used successfully for well over a decade in harsh oilfield environments. With this technique, the difference in optical density of the film in a noncorroded area of the image compared with the optical density in the pitted area can be correlated with the difference in thickness of the two areas, and thereby the pit depth is determined. With repeated surveys of specific areas on a frequency determined from the severity of the corrosion, the changing depth and area of corrosion can be readily resolved and corrosion rates calculated. The method can be used on-line but is too insensitive to provide real-time measurements.

Other Sources of Pertinent Information

ASME Boiler & Pressure Vessel Code, Section V (latest revision). "Nondestructive Examination." New York, NY: ASME.

ASME Boiler & Pressure Vessel Code, Section VIII, Division 1 (latest revision). "Rules for Construction of Pressure Vessels." New York, NY: ASME.

ASNT Recommended Practice No. SNT-TC-1A (latest revision). "Personnel Qualification and Certification in Nondestructive Testing." Columbus, OH: ASNT.

Benefits

The radiographic technique can be used to determine the integrity of piping and equipment over large areas relatively inexpensively, using either manual techniques or automated, real-time radiographic inspection systems. This technique does not require access to the component being inspected; therefore, insulated, clad, bundled, or otherwise inaccessible piping can still be inspected and the extent and severity of corrosion determined. Techniques can then be used to determine the integrity of the corroded piping directly.

Limitations

(a) Absolute thickness of the inspected object is not normally discernible from the radiographic image. From the differential optical density of the film, a difference in thickness (a pit depth) can be calculated, but the remaining wall thickness is assumed based on other information, such as the nominal wall thickness of the piping.
(b) The precision of the calculated thickness is not high. Field results have shown that the tolerance of the data is ±10% of the calculated pit depth in the best case.
(c) Scale or other debris in the area of corrosion can significantly affect the accuracy of the calculated pit depths.
(d) The radiographic source-to-detection distance is limited by the strength of the source. In field radiography, this limits the technique to use on piping and other objects with cross-sections of around a meter or less. The density of the product carried, the wall thickness of the material from which the pipe is made, and the type of source used to produce the ionizing beam also have a significant impact on the source-to-film or source-to-image distances that can be used.

3.1.6 Surface Activation and Gamma Radiometry

Definition and Scope

Gamma radiometry is a technique for determining metal loss by measuring the change in gamma radiation of a low level of radioactive tracer generated in a thin surface layer of the material to be monitored. The change in gamma radiation can be determined either by measuring the relative increase in gamma radiation in the process fluid removing the material or the relative loss of gamma radiation from the remaining material. The measured gamma radiation depends on the quantity of the original radioactive tracer present and the natural decay of the isotope with time (related to its half-life).

The technique is applied to measurements of wear, erosion, and corrosion when the corrosion product is removed from the surface. The generation of the radioactive tracer in the thin surface layer is used on coupons, sensors, or directly on plant components. Separate components in the system can be irradiated with different isotopes to allow measurements of each component at the same time. The technique can be used on-line to provide real-time measurements for relatively high metal-loss rates.

Other Sources of Pertinent Information

Asher, J., and T.W. Conlon. "Corrosion Monitoring in the Oil, Petrochemical and Process Industries." Ed. J. Wanklyn. London, UK: Oyez, 1982, p. 91.

Asher, J., S. Sugden, P.F. Lawrence, D.E. Williams, and C. Nash. "Comparison of Thin Layer Activation, Electrical Resistance and Electrochemical Techniques for Corrosion Monitoring in Cooling Water Plant." United Kingdom Atomic Energy Authority Report AERE R 12151. Harwell, England: AERE, 1986.

Characteristics of the Technique

(a) A small area on the inside of the vessel is irradiated to a thin layer, or a small specimen is similarly irradiated and used as an insertion specimen.
(b) Different thicknesses of the layer containing the tracer can be generated in the material to provide sensitivity to a wide range of corrosion rates, typically 20 to 200 µm (0.8 to 8.0 mils).
(c) The gamma radiation can penetrate typically up to 5 cm (2 in.) of steel with acceptable signal attenuation, so that on-site external monitoring of internally generated activated layers is possible without any physical interconnection between the internal and external surfaces.
(d) Compensation is typically made for gamma radiation decay of the tracer isotope with time (working life typically four to five times the isotope half-life from when first generated in the material).
(e) This technique is done at a suitable accelerator facility because of irradiation of material.
(f) To compensate for the natural isotope decay and the natural background levels, three measurements are used for each reading, namely the activated component, the reference sample of the same isotope (for natural decay), and the background radiation (for naturally occurring radiation in the system and atmosphere).
(g) Low levels of radiation present involve modest handling procedures. Product quality other than for human consumables is not compromised because dose rates are low and dilution of corrosion product reduces concentrations to very low levels.
(h) Sensitivity is greater than with ultrasonics but less than with electrical resistance.
(j) General characteristics of direct nonintrusive measurement techniques are given in the introduction to Section 3.

Benefits

(a) Activation area can be small (less than 1 mm² [0.002 in.^{2}]), which allows monitoring from specific metallurgical areas such as welds and weld heat-affected zones.
(b) Actual plant components such as impellers and valve seats can be activated.

Limitations

(a) This technique measures strictly material loss (it does not distinguish between erosion and corrosion). Corrosion products that are generated but still adhere to the material surface are not measured as material loss.
(b) Background levels of radioactivity in the process fluid can occasionally occur and can fluctuate, which causes interference with the measurement.
(c) Special handling procedures are used, though these are less stringent than those used for radiography.
(d) In most areas the technique probably requires licensing either the vendor or the user.

3.1.7 Electrical Field Mapping

Definition and Scope

Electrical field mapping is achieved by measuring local variations in voltage from an induced current applied directly to a pipe or structure to monitor changes due to the effect of internal or external cracking, pitting, corrosion, or erosion in the measurement area. The induced current is fed into the pipe, typically 3 to 10 m (9 to 30 ft) apart for a large pipe, or a few centimeters or inches for small pipes, to provide uniform current distribution. Welded, glued, or spring-loaded contact pins make electrical connections externally. The voltage readings are monitored and compared with one another to look at any nonuniformity that could be due to cracking or pitting in the monitored section. Comparison of the average voltage drop with that of a reference element (i.e., voltage or resistance ratio) is used to monitor general metal loss. In the latter form, the technique is similar to multiple electrical resistance probes except that the actual pipe or vessel is used as the measurement element, and using multiple taps creates multiple-measurement elements. The area monitored is dependent on the pin spacing. Increasing pin spacing reduces resolution for localized corrosion and increases resolution for general corrosion. Resolution of general corrosion is inversely proportional to wall thickness. This technique is used on-line to provide measurements of metal loss.

Other Sources of Pertinent Information

Strommen, R.D., H. Horn, and K.R. Wold. "FSM-A Unique Method for Monitoring Corrosion, Pitting Erosion and Cracking." CORROSION/92, paper no. 7. Houston, TX: NACE, 1992.

Characteristics of the Technique

(a) When a reference element is used, the measurement has a sensitivity to general metal loss of around one part per thousand of wall thickness.
(b) Pitting and cracking in the monitored area affect the voltage pattern between the monitored points according to their size and orientation.
(c) The type of flaw or metal loss is not identified by the technique, but in some cases can be interpreted from the data.
(d) The technique is easier to interpret if the specific type of flaw being monitored is known.
(e) General characteristics of direct nonintrusive measurement techniques are given in the introduction to Section 3.

Benefits

(a) The technique is useful in inaccessible areas because generally no access is required after initial installation.
(b) There are no consumable parts to the system except the pipe spool itself when used in high-corrosion-rate conditions.

Limitations

(a) This technique does not distinguish between internal and external flaws or general material loss. Typically monitoring of the internal surface is made, and the external surface is protected.
(b) The unit has a lower sensitivity when not permanently attached because of the need to relocate the contact pins accurately for voltage measurements.
(c) Discrimination between individual small pits is difficult or undetected because of the resolution between the welded attachments.
(d) Orientation of cracks affects detection sensitivity.
(e) Measurement sensitivity is not as high as with intrusive techniques for metal loss or electrochemical techniques.

3.2 Physical Techniques for Crack Detection and Propagation

3.2.1 Acoustic Emission

Definition and Scope

Acoustic emission (AE) monitoring is a technique that monitors the acoustic energy emitted by the microscopic growth of pre-existing flaws (e.g., stress corrosion cracks) as they propagate during stress changes due to some form of process excursion such as pressure or temperature. It is the flaw growth or even plastic deformation that generates the sound waves that are detected by the acoustic sensors. Secondary emissions from crack fretting or breaking of corrosion pockets can also be employed for detection of flaws. The technique is essentially qualitative in identifying areas with flaws that may be further investigated with other nondestructive techniques, usually ultrasonics.

Testing is most commonly done off-line by applying pressure changes, or during shutdown as the temperature is changing, to minimize the background effects of noise. On-line testing is also done, but the range of detection is reduced due to background noise. Frequency and gain of the sensors are modified according to the procedure to adjust filtering. Off-line tests are short-term tests to monitor for integrity. On-line tests are used to track the operational conditions that promote flaw propagation.

Normal frequency range of 150 to 175 kHz is used for initial wide coverage in off-line applications. For on-line applications in which flow noise is a problem, the frequency used is around 1 MHz, which reduces the range of coverage to about 0.50 m (1.5 ft). Statistical software techniques are used to reduce the interference of background noise.

AE monitoring has also been used for detection of actual leaks in structures such as the base of aboveground storage tanks where low frequency is used, and for slug detection in gas pipelines (see Flow Regime in Paragraph 4.4.1). The technique is used for off-line and on-line tests, and can be used for real-time measurements of crack growth.

Other Sources of Pertinent Information

API Publication 307. "An Engineering Assessment of Acoustic Methods of Leak Detection in Aboveground Storage Tanks." Washington, DC: API, 1992.

Davies, R. "Application of Real-Time Corrosion Surveillance Techniques to Process Industry Problems." CORROSION/91, paper no. 177. Houston, TX: NACE, 1991.

Characteristics of the Technique

(a) Each sensor location provides monitoring over an extended area depending on the frequency that can be used. At 175 kHz one sensor can cover a 6-m (20-ft) diameter vessel in an off-line test with a low background noise. At 1 MHz on-line, the coverage can be around 0.50 m (1.5 ft).
(b) In an off-line test with multiple sensors set to cover an entire structure, analysis can be achieved from a single test.

(c) Triangulation can be used to estimate the location of growing flaws.
(d) Acoustic energy measured at the sensor depends on the magnitude and distance of the flaw from the sensor.
(e) Typically, the maximum area that can be covered on-line from a single sensor is around 0.50 m (1.5 ft).
(f) The technique is qualitative and not quantitative.
(g) In off-line tests, care is used to generate temperature or pressure excursions representative of normal/adverse operating conditions.

Benefits

(a) The technique can be used for leak detection in aboveground storage tanks without draining the tanks.
(b) The technique can be used on plastics and steel.
(c) This technique can sometimes be used on-line based on amplitude to give a feedback alarm.

Limitations

(a) In off-line tests, overpressure only detects flaws that have sufficient energy at that time to be on the verge of propagation. It does not detect flaws that are not actively growing under the applied stress excursions, even though these flaws may be potential weak points or actively growing under a more severe process excursion.
(b) This technique does not give a quantitative indication of flaw magnitude.
(c) The technique produces large amounts of data and requires relatively sophisticated filtering analysis.
(d) When used for leak detection in aboveground storage tanks, this technique does not permit anticipation of imminent leaks.
(e) Reliability and accuracy of detecting small leaks is low.
(f) Interpretation of results highly dependent on skill, training, and expertise of personnel.
(g) Systems are not electrically intrinsically safe, which can be a problem for on-line use.

3.2.2 Ultrasonics (Flaw Detection)

Definition and Scope

Ultrasonics can be used to determine general metal loss within certain sensitivity levels as described in Paragraph 3.1.1. In addition, shear wave (angle beam) ultrasonics are sometimes used for flaw or crack detection, or with repeated readings, can be used to measure the propagation of such flaws. Many cracks are typically radial to the surface of pipes and vessels, so normal transducers on the surface can easily miss the interface. Shear wave measurements make use of transducers that send sound waves at an angle to the surface so that the sound waves are generally more perpendicular to the cracked interface and hence able to detect the interface. Orientation of the transducer to the direction of cracking is therefore important. A variety of cracking mechanisms such as fatigue, transgranular, intergranular, stress corrosion, creep, hydrogen embrittlement, and in-clad cracking, as well as other conditions, are detectable. In this form the technique is not normally used on-line and does not provide sufficient sensitivity to be considered as a real-time measurement. Ultrasonic pigs are being used on large pipelines for flaw detection.

Other Sources of Pertinent Information

ASME Boiler & Pressure Vessel Code, Section V (latest revision). "Nondestructive Examination." New York, NY: ASME.

ASME Boiler & Pressure Vessel Code, Section VIII, Division 1 (latest revision). "Rules for Construction of Pressure Vessels." New York, NY: ASME.

ASNT Recommended Practice No. SNT-TC-1A (latest revision). "Personnel Qualification and Certification in Nondestructive Testing." Columbus, OH: ASNT.

ASTM Special Technical Publication 908. "Corrosion Monitoring in Industrial Plants Using Non-Destructive Testing and Electrochemical Methods." Eds. P. Moran, and P. Labine. West Conshohocken, PA: ASTM.

Non-Destructive Testing Handbook, 2nd ed., vol. 7, Ultrasonic Testing. Section 17, "Ultrasonic Testing Applications in Utilities." Columbus, OH: ASNT, 1991.

Characteristics of the Technique

(a) This technique is used only when access to and physical contact with one surface of the component is possible.
(b) The material is typically capable of transmitting ultrasound energy. Most nonporous engineering materials are usable.
(c) Minimum flaw detection capability is dependent on the type of flaw and the examination technique. Detection of cracking that has a through-wall dimension of 1 to 5% of the component thickness is normally achievable.

Benefits

(a) This technique is capable of detecting and identifying many types of flaws including cracking, incomplete penetration, lack of fusion, slag, and porosity, as well as other conditions.
(b) Services and equipment are readily available in industry.
(c) It is a proven technique.
(d) Automated systems provide an easily understood visual display of examination results, which

typically include top, side, and end views, giving a better representation of the extent of the flaw.
(e) Automated system scanners can provide access to otherwise difficult or costly locations through the use of magnetic wheels or tracks.

Limitations

(a) Normally a calibration block of the same material as that being tested is used.
(b) Flaw orientation is critical. Conditions in which a sound beam can be oriented perpendicular to the major axis of the flaw are ideal. Flaws oriented parallel or nearly parallel to the sound beam sometimes are not detected.
(c) The technique can be either labor- or equipment-intensive.
(d) Trained experienced personnel, e.g., ASNT-certified, are required by some codes.
(e) The technique does not qualify as a corrosion-monitoring technique.

3.2.3 Ultrasonics (Flaw Sizing)

Definition and Scope

Ultrasonic sizing of the length and depth of flaws is accomplished using a variety of transducers and techniques. For decades the amplitude drop method was used for length and depth sizing. Since the mid-1980s, the amplitude drop method has been proved to be accurate for length sizing only. There is no one depth-sizing technique that is accurate through the full range of thicknesses encountered in industry. Multiple depth-sizing methods are normally utilized to assess crack depths accurately.

The available combinations of equipment and techniques make ultrasonics well-suited for crack depth sizing over a wide range of industry applications. Ultrasonic length and depth sizing examinations are common on a wide variety of aluminum, carbon steel, and stainless steel components in industry. Less common materials such as plastics and cast stainless steels can also be examined with special equipment.

Length sizing is typically accomplished using the amplitude drop method, in which the signal response drops off at the end of the crack. Crack length sizing can typically be performed using the same equipment that is used for crack detection.

Accurate crack depth sizing often uses special transducers and calibrations. The crack is typically first classified as shallow, mid-wall, or deep, then accurately sized with the appropriate equipment for the applicable range. In this form the technique is not normally used on-line and does not provide sufficient sensitivity to be considered as a real-time measurement.

Other Sources of Pertinent Information

ASME Boiler & Pressure Vessel Code, Section V (latest revision). "Nondestructive Examination." New York, NY: ASME.

ASME Boiler & Pressure Vessel Code, Section VIII, Division 1 (latest revision). "Rules for Construction of Pressure Vessels." New York, NY: ASME.

ASNT Recommended Practice No. SNT-TC-1A (latest revision). "Personnel Qualification and Certification in Nondestructive Testing." Columbus, OH: ASNT.

EPRI(7) CS-4774. "Guidelines for the Evaluation of Seam-Welded Steam Pipes." Palo Alto, CA: EPRI.

EPRI TM 911. "UT Operator Training for Sizing of IGSCC." Palo Alto, CA: EPRI.

Nondestructive Testing Handbook, 2nd ed., vol. 7, Ultrasonic Testing. Section 17, "Ultrasonic Testing Applications in Utilities." Columbus, OH: ASNT, 1991.

Characteristics of the Technique

(a) This technique depends on specialized training and experience to provide relatively accurate and consistent results.
(b) Access to and physical contact with one surface of the component is necessary.
(c) Through-wall depth sizing accuracy of ±1.3 mm (±0.050 in. [50 mils]) is normally achievable in the field.

Benefits

(a) Techniques and equipment are available to perform accurate depth determination over the full volume of a given component.
(b) Services and equipment are available in industry.
(c) This technique is proven and industry-accepted.

Limitations

(a) Special transducers and/or calibration blocks are sometimes needed.
(b) Weld crown preparation and/or access to both sides of a weld is sometimes necessary to determine the maximum depth of some cracks.
(c) Although this is a rare occurrence, some cracks cannot be accurately sized with existing techniques.
(d) This technique does not qualify as a corrosion-monitoring technique.

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(7) Electric Power Research Institute (EPRI), P.O. Box 10412, Palo Alto, CA 94303.

Section 4: Indirect On-line Measurement Techniques

4.1 Corrosion Products

4.1.1 Hydrogen Monitoring

Definition and Scope

Atomic hydrogen is generated at the cathode in some corrosion reactions, mainly in acidic environments. Atomic hydrogen (H_0) is a small enough atom to diffuse through metals, whereas molecular hydrogen (H_2) is not. Hydrogen probes monitor the proportion of that atomic hydrogen that permeates through a metal surface as distinct from the proportion that passes into the process stream. Various factors such as flow, velocity characteristics, temperature, contaminants present, and location affect the amount of hydrogen that enters the metal compared with that released to the process stream. For example, H_2S and arsenic in the process stream reduce the amount of hydrogen released to the process stream, forcing more into the metal. When the relative distribution is sufficiently constant, the permeating fraction of hydrogen can give relative corrosion rate information. The technique is used more commonly to detect high flow rates of hydrogen passing through the steel that are a direct cause of hydrogen blistering and hydrogen-induced cracking (HIC). The propensity of a metal to crack from HIC, however, varies substantially for different grades of metals. This technique is used on-line and can be used for real-time measurement. There are three principal types of hydrogen probes:

(a) Hydrogen pressure (or vacuum) probe: The insertion type of device consists of a steel tube or cylinder that includes an inner cavity. The pressure in the inner cavity of the tube or cylinder is measured with a pressure gauge. Patch-type devices, in which a patch or foil is welded or otherwise sealed to the outside of the pipe or vessel to create a cavity, are also available. These patch-type probes avoid insertion into the pipe or vessel. In some implementations, the pressure range from zero absolute to atmospheric pressure only is used, i.e., the vacuum region. Other types use positive pressure above atmospheric pressure only. Hydrogen passing through the wall of the tube or cylinder is detected as an increase in pressure in the cavity as a function of time. The higher the hydrogen flux, the greater the rate of pressure increases with time.

(b) Electrochemical hydrogen patch probe: This device is attached to the outer surface of the pipe or vessel to be monitored. The patch probe itself consists of a small electrochemical cell containing an appropriate electrolyte in contact with the item to be monitored. Typically, this cell uses the nickel electrode from a nickel cadmium battery with a caustic electrolyte put directly on the pipe. Often the electrolyte is isolated from the outer surface of the pipe or vessel by a thin palladium foil. This foil is also used as an electrode in the detection circuit. The cell is operated at a potential that oxidizes hydrogen as it enters the cell. The current used to maintain this potential is proportional to the hydrogen flux into the cell.

(c) Hydrogen fuel cell probe: This device consists of a small disc-shaped fuel cell. The cell contains a solid or gelled electrolyte, a cathode material, and a palladium foil anode. The electrolyte and cathode material have been chosen so that when hydrogen enters the cell through the palladium foil membrane, a chemical reaction takes place between the cathode material and the hydrogen, causing a current to flow in an external circuit between the cathode and palladium membrane. This current is directly proportional to the hydrogen flux through the palladium membrane. These cells are either mechanically attached to a pipe or vessel to be monitored, or attached directly to a specimen of the same or similar material as the process equipment and then inserted into the process flow as an insertion probe. As hydrogen passes through the pipe or vessel wall, it enters the palladium membrane and is detected as current in the external circuit. In this cell the hydrogen generates the current.

Other Sources of Pertinent Information

French, E.C. “Corrosion and Hydrogen Blistering Control in Sour Water Systems.” *Materials Performance* 17, 3 (1978): p. 20.

NACE Publication 1C184 (latest revision). “Monitoring Internal Corrosion in Oil and Gas Production Operations with Hydrogen Probes.” Houston,TX: NACE.

Uhlig, H.H. “Effect of Aqueous Sulfides and their Oxidation Products on Hydrogen Cracking of Steel.” *Materials Performance* 15, 1 (1976): p. 22.

Van Gelder, K., M.J.J. Simon Thomas, and C.J. Kroese. “Hydrogen Induced Cracking: Determination of Maximum Allowed H_2S Partial Pressures.” CORROSION/85, paper no. 235. Houston, TX: NACE, 1985.

Characteristics of the Technique

(a) Some types of hydrogen monitoring are nonintrusive and use the pipe or vessel wall as the test piece; others use an intrusive probe.
(b) The relationship of hydrogen flux to corrosion rate varies with the relative proportion of hydrogen passing into the steel compared with that released to the process stream.

(c) Hydrogen probes respond to changes in hydrogen flux in a few hours.
(d) Electrochemical hydrogen probes are very sensitive. Small amounts of hydrogen are detectable.
(e) Hydrogen measurements of this type apply only to the local area of measurement. The data are not always applicable to other parts of the system.
(f) On small electrochemical probes hydrogen can bypass the monitoring cell.
(g) The probe can be sensitive to hydrogen generated beyond the probe area.

Benefits

(a) The technique is useful when correlated with actual hydrogen blistering and HIC history to warn of hydrogen levels that can cause further damage.
(b) Some hydrogen probes are easy to relocate to various areas of interest.

Limitations

(a) The correlation between hydrogen flux and corrosion rate varies, because the amount of hydrogen passing into the steel compared with that being released into the process stream varies; hence, this technique may not provide a good measurement of corrosion rate.
(b) Hydrogen evolution does not apply to oxygen reduction in neutral or base solutions, so the technique is not considered suitable to indicate corrosion rates in these environments.
(c) Currently there is no known absolute correlation between hydrogen diffusion rates and corrosion rates, cracking, or blistering without specific analysis of a piece of the actual steel affected.
(d) Vacuum pressure systems operate only in the range of 0 to 101 kPa (0 to 14.7 psia [-14.7 to 0 psig]).
(e) Welded patch probes on vessels have sometimes required a stress relief heat treatment.
(f) Nonwelded patch probes can be difficult to keep sealed to hydrogen, and are limited to the maximum operating temperature of the seals.

4.2 Electrochemical Techniques

4.2.1 Corrosion Potential (E_{corr})

Definition and Scope

The corrosion potential (E_{corr}) is the potential of a corroding surface in an electrolyte relative to a reference electrode under open-circuit conditions (also known as *rest potential*, *open-circuit potential*, or *freely corroding potential*). The potential is normally measured relative to a reference electrode such as saturated calomel (SCE), silver/silver chloride (SSE), or copper/copper sulfate (CSE).

The value obtained is useful only if it is related to other measurements of the same phenomenon. The value is used to assist prediction of corrosion behavior by comparison with polarization data obtained from laboratory or site polarization scans. The corrosion potential is also useful in the development of information for use in conjunction with Pourbaix diagrams (E versus pH diagrams) of the environment and redox comparisons, etc. The corrosion potential can determine whether stainless steel is in the active or passive region. This technique is used on-line and can be used for real-time measurement.

Other Sources of Pertinent Information

ASTM C 876 (latest revision). "Standard Test Method for Half-Cell Potentials of Uncoated Reinforcing Steel in Concrete." West Conshohocken, PA: ASTM.

Betz Handbook of Industrial Water Conditioning. Trevose, PA: Betz Laboratories Inc., 1976.

Rossotti, H.S. *Chemical Applications of Potentiometry*. New York, NY: Van Nostrand, 1969.

Characteristics of the Technique

(a) This technique evaluates the region of the polarization diagram (E versus log I) in which a material is operating to help predict corrosion behavior, i.e., passivity, uniform corrosion, onset of pitting, and susceptibility to stress corrosion cracking.
(b) This technique is used to control cathodic and anodic protection systems, which hold the material at noncorroding or passive potentials.
(c) A reference electrode is used in this technique.
(d) This technique only indicates a corrosion risk and does not measure the corrosion or pitting rate.

Benefits

(a) This technique is a simple one that can be used to detect whether passivating alloys are in their passive region.
(b) Measurement enables one to assess whether a corrosion system is changing with time and how fast it is changing.

Limitations

(a) This technique does not measure any corrosion or pitting rates.
(b) The reference electrode itself can be unstable in the process stream.
(c) Reference electrodes can cause contamination.
(d) Special reference electrodes are used for operating temperatures above about 100°C (212°F).

4.3 Water Chemistry Parameters

All of the following measurements are used particularly in water treatment, and in general are only capable of being measured in aqueous environments. Many of these parameters are used in combination to generate various indices, such as the Langelier Index, to rate an overall calcium carbonate ($CaCO_3$) scaling tendency.

Other Sources of Pertinent Information

Betz Handbook of Industrial Water Conditioning, 9th ed. Trevose, PA: Betz Laboratories Inc., 1991.

Degremont, S.A. *Water Treatment Handbook* (translated from French into English by Language Consultants (France) Limited. New York, NY: Halsted Press, 1979.

Drew Principles of Industrial Water Treatment. Boonton, NJ: Drew Industrial Div., Ashland Chemical Co., 1995.

The NALCO Water Handbook, 2nd ed. Ed. F.N. Kemmer. New York, NY: McGraw-Hill Book Co., 1988.

4.3.1 pH

Definition and Scope

pH is defined as the logarithm of the reciprocal of the hydrogen ion activity [H^+]. pH denotes the hydrogen activity in solution. A value of 7.0 is neutral; values below 7.0 are increasingly acid; values above 7.0 are increasingly alkaline. A difference of 1.0 pH unit indicates a tenfold difference in hydrogen ion activity.

In general, for steel, low pH (or high acidity) produces a particularly corrosive environment. For other alloys this can vary.

pH is probably the single most important measure of corrosiveness of aqueous process streams toward plant materials. In many systems, though, pH is not the controlling factor in corrosion. This technique is used on-line for real-time measurement.

Relationship to Corrosion

(a) pH is an important corrosion factor for two reasons. First, the H^+ ion is a reactant for the cathodic reaction and drives the cathodic reaction at a certain pH. Secondly, the pH influences the solubilities of the products of the chemical corrosion reactions, particularly the passivation reactions involving oxides, sulfides, or carbonates.
(b) pH is an input variable into other indices, such as the Langelier Index, used in aqueous systems.

Other Sources of Pertinent Information

ASTM D 5464 (latest revision). "Standard Test Methods for pH Measurement of Water of Low Conductivity." West Conshohocken, PA: ASTM.

Ives, D.J.G., and G.J. Janz. *Reference Electrodes - Theory and Practice*. New York, NY: Academic Press, 1961. Reprinted by NACE with permission of Academic Press in 1996, Loc No. 60-16910.

Characteristics of the Technique

(a) pH is a measure of acidity or alkalinity of the process environment.
(b) pH is an important factor governing the chemical reactions that occur in the process stream and on the plant materials (e.g., Pourbaix diagrams, potential, pH, phase diagrams).
(c) As a measure of alkalinity, pH is a very important component in some indices such as the Langelier Index or Rysner Index.
(d) pH can be measured directly and continuously in-line or in side streams.
(e) Generally, pH measurements have been limited to a maximum temperature of approximately 99°C (210°F). Common pH probes have generally been limited to a maximum pressure of approximately 2 MPa (300 psig), although some special-purpose probes are available for up to 70 MPa (10,000 psi).
(f) Temperature is typically taken into account when interpreting and measuring pH.

Benefits

(a) pH measurement is a simple measurement.
(b) pH probes respond rapidly.

Limitations

(a) pH measurements can be inaccurate or meaningless in a strong salt solution in which sodium ion activity exceeds H^+ ion activity by a factor of 1×10^{10}.
(b) pH measurements can be affected by interfering ions such as lithium, sodium, and potassium ions. However, because lithium ions are normally not found in sample solutions and potassium ions cause little interference (because of their larger size), the most significant interference is from sodium ions.
(c) Frequent maintenance has often been necessary to ensure cleanliness and maintain calibration.
(d) Fouling of the probe measurement element (e.g., by hydrocarbons) can film over the surface, reducing the response or completely screening the probe's response to pH changes.
(e) Reference electrode fouling and interference can occur because buffers are used for reference electrodes in H_2S.
(f) Probe construction materials are often not compatible with the process stream.
(g) pH probes are relatively fragile.
(h) Low-conductivity solutions can be a problem. Even low-ionic-strength pH probes can have problems at conductivities less than 20 µS/cm (micromhos/cm). Some low-conductivity probes inject an electrolyte to correct for high solution resistance.

(i) Because a pH probe signal typically generates -410 mV to +410 mV for a range of 0 to 14 pH with 0 mV at 7 pH, a probe failure that results in no output gives an indication of 7 pH, which can cause difficulty in forming a valid reading.

4.3.2 Conductivity

Definition and Scope

Conductivity is the current-carrying capacity of a liquid, measured in terms of the current that flows when a constant potential is applied. The level of electrical conductivity is largely determined by the dissolved ionic solids concentration. Because corrosion is an electrochemical process, any increase in conductivity, in general, increases corrosion activity. However, this does not mean that zero electrolyte conductivity translates into zero corrosion. At some point, increased conductivity does not have a major impact for increased corrosion. This point varies greatly with other parameters affecting corrosion (e.g., redox potential, temperature, etc.). This technique is used on-line for real-time measurement.

Relationship to Corrosion

Conductivity is a function of the dissolved ionic solids in the process stream that can be a significant contribution to the corrosiveness of the process stream.

Other Sources of Pertinent Information

ASTM D 1125 (latest revision). "Standard Test Methods for Electrical Conductivity and Resistivity of Water." West Conshohocken, PA: ASTM.

Characteristics of the Technique

(a) This technique provides a general indication of the concentration of ionic species in liquid phase processes.
(b) This technique is sometimes used as a measurement of salinity in oil.
(a) This technique is an indirect measure of total dissolved electrolytes
(d) This technique can be used directly and continuously in-line or in side streams.
(e) Different measurement cells are used for different conductivity ranges.
(f) Conductivity measurements are generally made down to 1 µS/cm (or micromhos/cm). Below this value resistivity measurements are generally made.

Benefits

(a) This technique is a simple measurement.
(b) This technique is a rapid measurement.

Limitations

(a) Routine cleaning of the measurement cell has often been necessary to prevent false readings due to bridging of the electrodes, or fouling on the membrane.
(b) Electrochemical reactions at the electrode interfaces can affect the readings and can be dependent on the measurement frequency used (1,000 Hz is commonly used as the measurement frequency).
(c) The measurement is temperature-sensitive.

4.3.3 Dissolved Oxygen

Definition and Scope

Dissolved oxygen is the amount of oxygen dissolved in a liquid, usually expressed as parts per billion (ppb) or parts per million (ppm) in the engineering world to account for corrections in temperature and density changes, or milligrams per liter in the chemical world.

The solubility of oxygen depends on temperature, pressure, and molarity of the solution. It is generally employed as a measurement in an aqueous phase. Increased pressure increases oxygen solubility; increased temperature decreases oxygen solubility.

Dissolved oxygen can be measured by ion-selective electrodes, or for approximate low levels of oxygen a galvanic probe can be used (see Paragraph 2.2.1.2). The oxygen ion-selective electrode has a thin organic membrane covering a layer of electrolyte and two metallic electrodes. Oxygen diffuses through the membrane and is electrochemically reduced at the cathode. There is a fixed voltage between the cathode and anode so that only oxygen is reduced. The greater the oxygen partial pressure, the more oxygen diffuses through the membrane in a given time. The result is a current that is proportional to the oxygen in the sample. Temperature sensors can be built into the probe to make corrections for temperature of the sample and membrane temperature. The cathode current, sample temperature, membrane temperature, barometric temperature, and salinity information are used to calculate dissolved oxygen content of the sample in either concentration (ppb or ppm or mg/L) or percent saturation (% sat).

This technique is used on-line for real-time measurement.

Relationship to Corrosion

The affinity of oxygen for the common metals is the cause of many corrosion phenomena. Oxygen is responsible for both corrosive attack and passivation. Oxygen-provided corrosion is a process that ceases when oxygen is removed from the system. That does not mean that oxygen is always corrosive or that complete oxygen removal is always the only or best approach to controlling oxygen corrosion. The air saturation of water at 25°C (77°F) produces 5.756 cc/L of oxygen.

The approach to controlling corrosion of carbon steel in oil fields and in boilers in North America has generally been to remove all or most of the molecular oxygen by various combinations of physical and chemical means. Changes in oxygen levels below 20 ppb or 20 µg/L (20 x 10^{-9}) have a significant effect on corrosion. With an oxygen scavenger, typical levels are below 1 ppb or 1 µg/L.

In some boilers that use high-purity deionized water, no oxygen scavengers are used and small amounts of molecular oxygen or hydrogen peroxide are deliberately added to the feedwater instead. In this approach, the oxidant acts as a passivating agent for carbon steel under carefully controlled conditions of boiler water chemistry. Some deaeration has sometimes been necessary, however, to achieve the desired levels of around 0.02 to 0.2 ppm or 0.02 to 0.2 mg/L (25°C [77°F]).

For applications in which dissolved oxygen contributes to corrosion or acts to passivate carbon steel, dissolved oxygen levels can be monitored on-line to indicate the tendency for corrosion. In some instances, such as applications in which stainless steel is used, oxygen has been necessary initially to permit reformation of the passive film.

Characteristics of the Technique

(a) Dissolved oxygen is involved in many corrosive processes and has an effect on the corrosiveness of the process environment, depending on the temperature.
(b) Measurements can be made directly and continuously in-line or on side stream.
(c) Generally, dissolved oxygen measurements have been limited to a temperature maximum of 65°C (150°F) and a pressure maximum of 200 to 350 kPa (30 to 50 psig). However, pulsing (pressure fluctuations) is avoided.
(d) Consumption of oxygen by the probe causes a lowering of the oxygen concentration, so that a flowing or stirred sample has generally been used.
(e) The electrolyte becomes depleted as it reduces the oxygen and is replaced, typically in two weeks to six months, depending on the design and use of the probe.
(f) Periodic calibration of the probes has generally been performed.

Benefits

Changes in dissolved oxygen are good indicators of impending operational or corrosion problems.

Limitations

(a) Poisoning of the electrode can occur. This has precluded the use of the method in many industrial environments such as processes involving heavy hydrocarbon and water. Typical uses have been boilers and cooling water systems.
(b) Other dissolved gases, such as hydrogen and carbon dioxide (CO_2), can interfere with the measurement.
(c) In high-pressure process streams, a reduced-pressure side stream has sometimes been used for measurement of dissolved oxygen. The pressure reduction can affect the dissolved oxygen remaining in solution.
(d) Regular maintenance has been performed because of fouling of the membrane and electrode.
(e) The normal failure mode results in erratic readings, usually as a result of membrane failure.

4.3.4 Oxidation Reduction (Redox) Potential

Definition and Scope

Oxidation reduction (redox) potential is the potential of a reversible oxidation-reduction electrode measured with respect to a reference electrode, corrected to the hydrogen electrode, in a given electrolyte. The measurement system comprises a sensitive voltmeter connected between a reference electrode and a noble metal sensing electrode. The change in potential of the sensing electrode, produced by the oxidizing or reducing species, is measured relative to the stable reference electrode. This output is then converted electronically to display on a meter or recorder. This technique is used on-line for real-time measurement.

Relationship to Corrosion

This technique can be used to detect the end point of oxidation or reduction reactions. In water treatment the technique can be used to control more closely the addition of oxidizing biocides, such as chlorine and bromine, which also have a significant effect on corrosion rates.

Other Sources of Pertinent Information

Ewing, G.W. *Instrumental Methods of Chemical Analysis*. New York, NY: McGraw-Hill Inc., 1985, p. 271.

Strand, R.L. “Optimization of Redox for Bromine/Chlorine Control.” CORROSION/91, paper no. 269. Houston, TX: NACE, 1991.

Characteristics of the Technique

(a) The measurement is made in a conductive environment, normally water.

(b) The measurement is similar to a pH measurement.
(c) This measurement can be used to complement other measurements.
(d) The platinum sensing electrode is typically of high purity.
(e) Coatings are often used on the platinum electrode to prevent hydrogen overvoltage errors.
(f) Special reference cell gels are used to reduce degradation by the oxidizing agent.

Benefits

(a) This measurement can be used for control of chemical additives.
(b) This measurement can serve as a rough indicator of the corrosiveness of the solution.
(c) This technique can be used in the measurement of microbiological activity.

Limitations

(a) Measurements can be affected by interfering ions.
(b) Probe contamination can affect the response of the platinum electrode probe; the probe sometimes needs to be cleaned manually.
(c) Contamination of the reference electrode can occur.

4.4 Fluid Detection

4.4.1 Flow Regime

Definition and Scope

Flow regime can be important in two aspects. In single-phase flows, the flow regime is typically described as laminar, transition, or turbulent flow as defined by the Reynolds number, which depends on the flow velocity, the pipe diameter, the fluid viscosity, and the fluid density. In multiphase flows the relative pattern of multiple phases is important as defined by mist flow, annular flow, or slug flow. In single-phase environments the flow regime affects the mass transfer to the metal surface and the shear stresses on the metal surface. These have a direct impact on the corrosion rates at the metal surface. In multiphase flows the flow regime varies with varying flow rates of each phase, elevation changes, or specific geometry of a line. Acoustic monitoring and on-line γ-radiography have been used to detect slug flow. Flow detection has also been used to guard against flooding of vessels that would otherwise be dry and possibly create corrosive conditions with acid gases. The flow characteristics can also be used to provide predictions of corrosion rates based on modeling and other empirical data (see [e] in Other Sources of Pertinent Information).

In single-phase flows with velocity-assisted corrosion, where the corrosion process is limited by diffusion control, the corrosion rate of dissolution per unit area (R) can be expressed as shown in Equation (1):

$$R = K_1 (C - C_0) \tag{1}$$

where C = concentration of the corrosion product at the surface
C_0 = concentration of the corrosion product in the bulk solution
K_1 = mass transfer coefficient

It is convenient to express K_1 in a dimensionless format. The dimensionless mass transfer number, or Sherwood number, is defined in Equation (2):

$$Sh = K_2 d/D \tag{2}$$

where d = the characteristic dimension of the system
D = the diffusion constant of the material diffusing
K_2 = constant for the equation

In general, the Sherwood number is determined by the flow conditions in a specific geometry system by an equation of the type shown in Equation (3):

$$Sh = k_3 Re^a Sc^b \tag{3}$$

where k_3 = constant for this equation
Re = Reynolds number
Sc = Schmidt number
a, b = constants for the system

In multiphase flows, predictive models based on dimensionless shear stress (Froude number) have been used to predict areas of more severe velocity-assisted corrosion.

Relationship to Corrosion

(a) Corrosion usually occurs on the metal surface wetted by the aqueous phase. This wetting action and transport of corrosive agent to the surface can be controlled by the flow regime.
(b) Some flow regimes, such as slug flow, can generate high surface shear stresses and extreme turbulence. Such conditions can make inhibition difficult and can create corrosion rates of several hundred millimeters (several thousand mils) per year.
(c) Impingement, cavitation, and erosive conditions created by two-phase flows can be extremely corrosive.

Other Sources of Pertinent Information

Brill, J.P., and H. Beggs. “Two Phase Flow in Pipes,” 3rd ed. Tulsa, OK: University of Tulsa, 1977.

Dean, S.W. "Velocity-Accelerated Corrosion Testing and Predictions - An Overview." *Materials Performance* 29, 9 (1990): p. 61.

Heitz, E. "Chemo-Mechanical Effects of Flow on Corrosion." CORROSION/90, paper no. 1. Houston, TX: NACE, 1990.

Johnson, B.V., H.J. Choi, and A.S. Green. "Effects of Liquid Wall Shear Stress on CO_2 Corrosion of X-52 C-Steel in Simulated Oilfield Production Environments." CORROSION/91, paper no. 573. Houston, TX: NACE, 1991.

Taitel, Y., and A.E. Dukler. "A Model for Predicting Flow Regime Transitions in Horizontal and Near Horizontal Gas-Liquid Flow." *AIChE Journal* 22, 1 (January 1976): p. 47.

Benefits

(a) For single-phase flows, predictive empirical models can be used to estimate likely corrosion rates.
(b) For multiphase flows, predictive models can be used to estimate the location of more corrosive areas if the nature of the corrosive attack and the characteristics of the adverse flow conditions have been established.
(c) The determination of flow regime assists in predicting the location of more corrosive areas if the nature of the corrosive attack and the characteristic of the adverse flow conditions have been established.
(d) Measurement of frequency of slugs of liquid flow can help predict likely corrosion rates if the measured effect of typical slugs is known for that environment.

Limitations

It is not a "measurement" technique, only an indication of a problem area or frequency of a problem. This technique relies on a thorough understanding of the precise corrosion mechanisms as they occur in process streams. This can sometimes enable monitoring of the vital characteristics of the corrosiveness of the flow.

4.4.2 Flow Velocity

Definition and Scope

In single-phase flow, the velocity is easily determined from the mass flow rate using appropriate corrections for pressure and temperature. In multiphase flow, the velocity is more difficult to determine due to slip between the phases, and the velocity is often not constant. Correlations can be used to estimate the slip and determine flow velocities for each phase. This technique is used on-line for real-time measurement.

Relationship to Corrosion

(a) Flow velocity has a strong influence on corrosion rates. The most severe corrosion has often occurred at extremes of velocity, i.e., stagnant conditions, or velocities two or three times higher than API RP 14E[10] limits. Flow/no-flow detection can be used, particularly when oxygen content is important to corrosion. In other instances, orifices can be used to create a minimum or maximum flow.
(b) In multiphase flow, the relationship between corrosion and velocity is often not direct due to the effects of flow regime and phase transport (see Paragraph 4.4.1 on Flow Regime).

Other Sources of Pertinent Information

API RP 14E. "Recommended Practice for Design and Installation of Offshore Production Platform Piping Systems." Washington, DC: API.

Brill, J.P., and H. Beggs. "Two Phase Flow in Pipes," 3rd ed. Tulsa, OK: University of Tulsa, 1977.

Govier, G.W., and K. Aziz. "The Flow of Complex Mixtures in Pipes." New York, NY: Van Nostrand, Rheinhold, 1972.

Kennelley, K.J., R.H. Hausler, and D.C. Silverman, eds. *Flow-Induced Corrosion: Fundamental Studies and Industry Experience*. Houston, TX: NACE, 1992.

Benefits

Flow velocity can be related to the measured corrosion rate so that operating limits or guidelines that prevent excessive corrosion rates can be set.

Limitations

(a) The method is useful only as long as the corrosive environment of the process stream remains relatively constant.
(b) The flow velocity measurement in multiphase flows is more complex than in a single-phase flow.
(c) It is only applicable for corrosion conditions in which flow velocity is a significant factor.

4.5 Process Parameters

The following parameters are all mathematically related to fluid hydrodynamics and fluid mass transfer properties, which in turn have a direct bearing on the corrosiveness of the fluid.

4.5.1 Pressure

Definition and Scope

Pressure can affect the proportion of phases that are present in a vessel or pipe, or the composition of the process. Different phases and constituents can produce quite different corrosive environments. For example, the partial pressure of CO_2 affects the amount of CO_2 dissolved in water, which in turn affects the corrosiveness of the fluid due to the presence of carbonic acid. Similarly, the partial pressure of H_2S is a major determining factor in the susceptibility of various alloys to sulfide stress cracking (SSC). Total pressure measurements can be made on-line, and are a real-time measurement. Determination of partial pressures utilizes knowledge of the composition of the process fluid, the temperature, and the total pressure. This involves sampling of the process fluid.

Other Sources of Pertinent Information

NACE Standard MR0175 (latest revision). "Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment." Houston, TX: NACE.

Relationship to Corrosion

In some gas/liquid systems, pressure affects gas solubility, but the relationships are complex. Consequently, the pressure is usually used only to analyze and predict which phases are present, rather than as an on-line measurement.

Benefits

(a) It is a simple measurement to make.
(b) It can be used to set operating limits for the prevention of excessive corrosion rates.

Limitations

The technique is only applicable when pressure has a significant effect on the corrosive environment.

4.5.2 Temperature

Definition and Scope

The temperature of a process fluid can have a direct effect on its corrosiveness. These temperature effects can be nonlinear. Low temperature can produce condensation of water or other corrosive liquids. High temperature increases chemical reaction rates and can change the composition of the process. As a process measurement, this technique is used on-line for real-time measurement.

Relationship to Corrosion

Temperature directly affects corrosion dynamics. In general, increased temperature increases the chemical reaction rates. The temperature can lead either to vaporization (a dry condition) or condensation (from a dry to a wet condition). Both of these changes in state can affect corrosion.

Benefits

(a) The measurement is simple to make.
(b) It can be used to set operating limits for the prevention of excessive corrosion rates.
(c) The corrosion rates of most environments change with temperature.

Limitations

The technique is not applicable when processes do not change temperature, or temperature does not have a significant effect on the corrosive environment.

4.5.3 Dewpoint

Definition and Scope

Dewpoint is the temperature at which the liquid concerned (commonly but not necessarily water) begins to condense. This can be complex in some environments where multiple gases and condensible combinations are present. In atmospheric environments the dewpoint is measured with a wet-bulb thermometer. In a process system this may not be practical, and a system in which cooling of the flow to the point of condensation on an optical mirror has been used. The direct effects of dewpoint conditions can be measured with mass-loss coupons or electrical resistance techniques (see Paragraphs 2.1.1 and 2.1.2). Electrochemical methods can also sometimes be used in a similar way, either as a time-of-wetness indicator or for corrosion rate measurements if the measurement surfaces are continuously and completely wetted. Additionally, forced cooling of the corrosion-measurement surfaces can be used to generate the appropriate dewpoint on the measurement surfaces. This technique can be used on-line for real-time measurement.

Relationship to Corrosion

Dewpoint is important because the region of condensation of water and corrosive fluids in otherwise dry environments has a major impact on corrosion rates.

Other Pertinent Sources of Information

ASTM G 84 (latest revision). "Standard Practice for Measurement of Time-of-Wetness on Surfaces Exposed to Wetting Conditions as in Atmospheric

Corrosion Testing." West Conshohocken, PA: ASTM.

Benefits

(a) For water condensation in atmospheric environments, it is a relatively simple measurement to make in atmospheric environments where corrosion is to be measured.
(b) It is a measurement made of corrosive versus noncorrosive condition for water condensation. For a relatively uniformly corrosive process, time-of-wetness enables an estimate of total corrosion that has occurred to be made.

Limitations

(a) Dewpoint is more difficult to measure in process environments at other than atmospheric conditions.
(b) This technique is only applicable to gases in which condensation may occur.
(c) It is hard to tell whether the thermal characteristics monitoring arrangement is a realistic representation of those of the process equipment. As a result, a vast under- or over-assessment of corrosion rates can be produced.

4.6 Deposition Monitoring

4.6.1 Fouling

Definition and Scope

Fouling is an accumulation of deposits. It includes the accumulation and growth of microbiological organisms on a submerged metal surface and the accumulation of deposits on heat exchanger tubing. For the purposes of this report, fouling can be considered as the deposition of both organic and inorganic substances from a fluid stream onto the surfaces of the equipment through which the fluid is passed, as well as in situ corrosion products and inorganic deposits such as hardness salts that occur on the metal surface. Further, fouling is limited to those substances that either restrict flow by causing an increase in pressure drop through the equipment or retard heat transfer by formation of an insulating deposit. This technique is used on-line, or in a side stream for real-time measurement.

Side-stream and in-line intrusive measurement techniques, together with visual inspection, have been used for determination of fouling. One of two techniques has been employed—heat transfer monitoring or pressure-drop monitoring.

Relationship to Corrosion

(a) Fouling is important relative to underdeposit corrosion because it causes highly anodic areas.
(b) Fouling can give rise to hot spots in boilers.

Other Sources of Pertinent Information

NACE Standard RP0189 (latest revision). "On-Line Monitoring of Cooling Waters." Houston, TX: NACE.

NACE Standard TM0286 (latest revision). "Cooling Water Test Unit Incorporating Heat Transfer Surfaces." Houston, TX: NACE.

Characteristics of the Technique

Devices are normally operated on a side stream.

Benefits

(a) Monitoring of fouling provides a general indication of deposition, which in turn can indicate potential for underdeposit corrosion in systems such as cooling water.
(b) Steady-state conditions can be set up for test and evaluation on the actual process fluid; that may not be possible in the actual operating equipment.
(c) This technique is not limited to evaluating a single velocity profile or heat transfer condition.
(d) This technique can be used to evaluate alternate operating strategies (play "what if's").

Limitations

(a) Accepted techniques are commercially available only for aqueous systems and flue gases.
(b) Different monitoring techniques are used for nonaqueous systems.

4.7 External Monitoring

4.7.1 Thermography

Definition and Scope

Thermography is the determination of temperature remotely by optical measurement of thermally radiated energy. Areas with significant temperature variations can be readily identified by measuring the thermal radiation caused by the temperature of the process equipment. Thermal radiation of process equipment depends on many factors and among these, the effect of the thickness of the metal or the presence of a corrosion scale is relatively small. Even the qualitative assessment of corrosion can be questionable. This technique has been used to detect hot spots resulting from failures in the refractory linings of, for example, furnaces or regenerators of fluid catalytic cracking units (FCCU), and for detecting failure of thermal insulation for cold or hot equipment.

Characteristics of the Technique

(a) Temperature differences can be readily detected.

(b) The technique can be used for process plants in which insulation is used to protect the metal from either high or low temperatures. Failure of such protection causes localized temperature changes in the metal.

Benefits

(a) The technique has been used to detect hot spots resulting from failures in the internal refactory linings of, for example, furnaces or regenerators of fluid catalytic cracking units.
(b) The failure of thermal insulation in hot or cold equipment can be detected. Loss of thermal insulation in cold equipment can give rise to condensation and subsequent corrosion.

Limitations

The technique does not directly detect areas of corrosion or thinning. Thermal radiation depends on many factors and among these, the effect of the thickness of metal or presence of corrosion scale are relatively small. Even qualitative assessment of corrosion can be questionable.

Section 5: Indirect Off-line Measurement Techniques

5.1 Water Chemistry Parameters

5.1.1 Alkalinity

Definition and Scope

Alkalinity is a measure of the acid-neutralizing capacity of water. In natural water, it usually consists of hydroxide (OH^-), carbonate (CO_{3-}^{2}), and bicarbonate (HCO^{3-}) species. Alkalinity is affected by contact with air through CO_2 absorption. Alkalinity is measured because carbonate and hydroxide scales are common problems. This technique is not used on-line or for real-time measurement.

Relationship to Corrosion

(a) Alkalinity is a solution variable that is dependent on the environment and has relevance to other parameters and to corrosion.
(b) Alkalinity measurement has normally been used in combination with other measurements to characterize solution and physical characteristics.
(c) Alkalinity affects fluid chemistry.
(d) Alkalinity can be integrated in a chemical balance for total metal loss in low corrosion rates (used in the nuclear industry).

Benefits

It is useful in treatment of water to prevent corrosion where acid additions may occur, to assure correct neutralization occurs and the desired pH is achieved.

Limitations

(a) It is a normally a laboratory analysis, so that it is not an immediate measurement.
(b) It is limited to water systems.
(c) It is useful only when acid neutralization is involved in the corrosion control.

5.1.2 Metal Ion Analysis

Definition and Scope

Metal ion analysis of a process stream is used as a technique for determining the amount of metal lost that has dissolved in the process stream or that has been carried along in the process stream as corrosion product (e.g., iron, copper, nickel, zinc, manganese). Analysis has routinely been performed by some users. This technique is not used on-line or for real-time measurement.

Relationship to Corrosion

Some corrosion products are soluble and can be detected by metal ion analysis of the process stream.

Other Sources of Pertinent Information

NACE Standard RP0192 (latest revision). "Monitoring Corrosion in Oil and Gas Production with Iron Counts." Houston, TX: NACE.

Characteristics of the Technique

(a) This technique is most useful when applied to closed systems, if corrosion products are soluble or relate to particular concentrations.
(b) In open systems, changes in concentration from one location to another are most accurate.
(c) Much care is used in obtaining a representative sample of the aqueous phase, including the sampling point design, because the sampling point can accumulate corrosion products.
(d) Iron counts are related to flow rates of water to determine changes in corrosion rates.
(e) A history is established to interpret the data.

Benefits

The analysis can be done easily, inexpensively, and quickly in the field.

Limitations

(a) In open systems, single-point monitoring (e.g., at wellheads) can reflect changes in corrosion rate upstream (downhole), but the input flow affects the results.
(b) An assumption is made that metal loss occurred over the total surface area, and that the concentration of ions in solution is proportional to the corrosion rate. This is sometimes very unrepresentative and only a trend indication.
(c) Precipitation upstream from the sample affects the measurement.
(d) Obtaining a representative sample from a process stream can be difficult, because velocity is different, and the temperature and pressure can be different unless specific precautions are taken to prevent this.

Additional Limitations of Iron Counts

(a) The technique is generally not reliable in sulfide-containing fluids because of precipitation of iron sulfide, or in alkaline solutions because of precipitation of ferric hydroxide.
(b) Corrosion of the sample container can contribute to the iron count.
(c) Increased activity level of sulfate-reducing-bacteria (SRB) can reduce the iron count by increasing the precipitation of iron sulfide.
(d) An increase in the metal ion concentration can indicate an increase in corrosion. A low metal ion concentration is not a guarantee of low corrosion, due to the possibility of localized corrosion, deposition of the metal ion due to temperature or pH changes, or a significant time delay before analysis.
(e) This technique can only be related directly to corrosion rates in special circumstances.

5.1.3 Concentration of Dissolved Solids

Definition and Scope

Total dissolved solids (TDS) is the sum of minerals dissolved in water. TDS is determined by evaporating the water from a preweighed sample. A calculated TDS value can be determined by adding the various cations and anions from an analysis. This technique is not used on-line or for real-time measurement.

Relationship to Corrosion

(a) The concentration of dissolved solids relates directly to conductivity.
(b) Dissolved ionic solids affect fluid chemistry.
(c) The measurement is typically used in conjunction with other parameters.

5.1.4 Gas Analysis

Definition and Scope
Gas analysis is generally done in a laboratory, but can also be done for certain gases in the field. The analysis commonly includes hydrogen, H_2S, or other dissolved gases. This technique is not used on-line or for real-time measurement.

Relationship to Corrosion

(a) This technique is used to determine potentially corrosive constituent gases, particularly acid gases, that become corrosive when hydrated or the temperature falls below the dewpoint.
(b) This technique is used in the analysis of gaseous corrosion products (e.g., hydrogen).

Benefits

For situations in which acid gases are present and may be condensed to liquid form, it can be a useful indicator of corrosion risk.

Limitations

(a) It is limited to very specific gaseous process situations.
(b) The equipment for analysis is relatively expensive.
(c) The maintenance on the analytical equipment is relatively high, especially for plant equipment.

5.1.5 Residual Oxidant

Definition and Scope

Ozone and halogens, specifically chlorine, chlorine dioxide, and bromine, are powerful oxidizing agents. Residual halogen can directly oxidize the inhibitors used to protect against corrosion or fouling. Chlorine and bromine are widely used to control microbiological fouling in aqueous systems. Halogens in aqueous solutions can be measured using redox potential or one of a variety of colorimetric techniques. Halides are salts that come from halogen acids, typically HF, HCl, HBr, and HI. Halides have been directly implicated as a causative agent in SCC. Halides have been indirectly linked to galvanic corrosion by increasing conductivity (see Paragraph 4.3.2). Halides can be measured using specific ion electrodes or colorimetrically. This technique is not used on-line or for real-time measurement.

Other Sources of Pertinent Information

AWWA(8) *Standard Methods for Examination of Water and Waste Water*. Denver, CO: AWWA.

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(8) American Water Works Association (AWWA), 6666 W. Quincy Ave., Denver, CO 80235.

Benefits

(a) The techniques of analysis are relatively simple.
(b) The techniques are directly applicable to the actual system evaluation.
(c) The measurements can be used to provide automated control.

Limitations

(a) The measurement is made by side-stream sampling.
(b) The technique is applicable only in aqueous solutions.
(c) There is no direct correlation between concentration of oxidant and corrosion rate.

5.1.6 Microbiological Analysis

Definition and Scope

There are a variety of techniques available for microbiological analysis. In all the cases, a sample is taken and then the analysis is made. The most common and most developed technique of analysis is bacterial culturing from the sample to determine the concentration of viable bacteria. Successive dilutions of the sample are put into the culture media and left to grow. The samples that develop give an indication of the original concentration of bacteria. The test can show some results in a few days, but the usual incubation period for the test is 14 to 28 days. This technique is not used on-line or for real-time measurement.

New techniques for rapid determination of bacterial populations and bacterial activity are under development. Some of the general bacteria techniques are as follows:

(a) Adenosine Triphosphate (ATP) Photometry — Measurement of ATP present in all living cells, but which disappears rapidly on death, can be used as a measurement of living material. The ATP can be measured using an enzymic reaction, which generates flashes of light that are detected by a photomultiplier.

(b) Fluorescence Microscopy — The total number of viable bacteria can be determined by using specific stains that fluoresce when irradiated with ultraviolet light. The technique is usually performed in the laboratory.

(c) Hydrogenase Measurement — The test analyzes for the hydrogenase enzyme that is produced by bacteria able to use hydrogen as an energy source. Because cathodic hydrogen is believed to be an important factor in microbiologically influenced corrosion (MIC), the test can indicate a potential for this type of corrosion. The test is usually performed on sessile samples. The sample is exposed to an enzyme-extracting solution, and then the degree of hydrogen oxidation in an oxygen-free atmosphere, as detected by a dye, is noted.

Some rapid techniques are used to measure sulfate-reducing bacteria (SRB) as follows:

(a) Radiorespirometry — This technique is specific to SRBs. It depends on bacterial growth for detection, but it generates results in about two days. The sample is incubated with a known trace amount of radioactive-labeled sulfate. (SRBs reduce sulfate to sulfide.) After incubation, the reaction is terminated with acid to kill the cells and the radioactive sulfide is fixed in zinc acetate and then sent to a laboratory to be quantified. This is a highly specialized technique, involving expensive laboratory equipment and the handling of radioactive substances.

(b) Antibody Fluorescence Microscopy — This technique is similar to general fluorescent microscopy, except that the fluorescent dye used is bound to antibodies specific to SRBs. Only bacteria recognized by the antibodies fluoresce. Results can be analyzed within two hours. The technique detects viable and nonviable bacteria. The technique detects only the type of SRB used in the manufacture of these antibodies.

(c) Adenosine Phosphosulfate (APS)-Reductase Measurement — This technique takes advantage of the fact that SRBs reduce sulfate to sulfide through the presence of an enzyme, APS-reductase, common to all SRBs. Measurement of the amount of APS-reductase in a sample gives an estimate of total numbers of SRBs present. The test does not require bacterial growth and the entire test takes 15 to 20 minutes.

Relationship to Corrosion

Bacteria in a system can be either in suspension in the fluid (planktonic) or attached to the surface (sessile). The sessile bacteria are the only ones that are relevant to corrosion or MIC. The presence of bacteria does not necessarily indicate they are causing a problem. Bacteria that may be a problem in one system may be harmless in another.

Other Sources of Pertinent Information

API RP 38 (latest revision). “Recommended Practice for Biological Analysis of Subsurface Injection Waters.” Washington, DC: API.

Hardy, J.A., and K.R. Syrett. “A Radiorespirometric Method for Evaluating Inhibitors of Sulfate-Reducing Bacteria.” *European Journal of Applied Microbiology and Biotechnology* 17 (1983): pp. 49-51.

Horacek, G.L., and L.J. Gawel. "New Test Kit for Rapid Detection of SRB in the Oilfield." Paper no. SPE 18199, 63rd Annual Technical Conference of the Petroleum Engineers. Richardson, TX: SPE,(9) 1988.

Littmann, E.S. "Oilfield Bactericide Parameters as Measured by ATP Analysis." International Symposium on Oilfield Chemistry, paper no. 5312. Dallas, TX: SPE, 1975.

Microbiologically Influenced Corrosion and Biofouling in Oilfield Equipment, TPC #3. Houston, TX: NACE, 1990.

"Microbiological Methods for Monitoring the Environment Water and Wastes." Cincinnati, OH: U.S. Environmental Protection Agency, 1978.

NACE Standard TM0173 (latest revision). "Methods for Determining Water Quality for Subsurface Injection Using Membrane Filters." Houston, TX: NACE.

Pope, D.H., and T.P. Zintel. "Methods for the Investigation of Under-Deposit Microbiologically Induced Corrosion." CORROSION/88, paper no. 249. Houston, TX: NACE, 1988.

Prasad, R. "Pros and Cons of ATP Measurement in Oil Field Waters." CORROSION/88, paper no. 87. Houston, TX: NACE, 1988.

Rosser, H.R., and W.A. Hamilton. "Simple Assay for Accurate Determination (^{35}S) Sulfate Reduction Activity." *Applied and Environmental Microbiology* 6, 45 (1983): pp. 1956-1959.

"Standard Methods for Examination of Water and Wastewater," 17th ed. Washington, DC: American Public Health Association, 1989.

Characteristics of the Techniques

(a) All of the techniques use sampling. The technique of sampling is important to obtaining representative measurements.
(b) Different techniques measure different aspects of the bacterial process or bacterial presence.
(c) Some techniques measure viable bacteria, while others measure viable and nonviable bacteria.

Benefits

(a) The techniques give an indication of the effectiveness of biocide treatments to kill bacteria.
(b) Measurement of sessile bacteria can give an indication of the potential for MIC.
(c) Rapid techniques sometimes have qualifications, but rapid results permit remedial action to be taken in a timely manner.

Limitations

(a) The presence of bacteria does not necessarily mean MIC is occurring.
(b) The culture techniques are slow, requiring up to 28 days for analysis.
(c) The slow analysis does not permit real-time control of a biocide.
(d) Even rapid techniques require manually collected samples for analysis, which prevents automatic or remote operation.

5.2 Residual Inhibitor

Definition and Scope

Measurement of corrosion inhibitor residuals in a system provides an indication of the presence of pre-selected concentrations of inhibitor at various locations in the system. This technique is not used on-line or for real-time measurement.

Characteristics of the Technique

(a) Test methods measure the quantity of inhibitor that reaches a given sample point in a system.
(b) Analytical results are reliant on the ability to obtain a representative sample of the test fluid (oil, water, or gas) in a suitable container that does not absorb or react with the inhibitor in use.
(c) Test methods can be used to determine whether sufficient mixing or agitation occurs to disperse the inhibitor properly in the test media. Sometimes inhibitor reacts with, or is removed from, test fluids in large quantities by products in the system.
(d) System design is generally such that inhibitor is carried through the system to the sampling location in the system fluid (gas or liquid) without dropout in low spots, removal at splits, or fluid withdrawal points upstream from the sample location.

Benefits

(a) When the reliability of an analytical test method is established and the minimum acceptable inhibitor concentration has been determined, measurement of inhibitor concentrations throughout the system can indicate whether adequate corrosion protection is likely to be achieved at each sample location.
(b) Inhibitor loss due to reaction with the system hardware or reaction with the environment (absorption, neutralization, precipitation, adsorption on solids or corrosion products) can be detected and compensated for in dosage selection.

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(9) Society of Petroleum Engineers (SPE), 222 Palisades Creek Dr., Richardson, TX 75083-3836.

(c) Inhibitor injection points can be evaluated and the number of injection points can be determined for lengthy or complex systems by measurement of carry-through of inhibitor.

(d) Inhibitor selection can be carefully refined after selection of potential candidates by determining which products are transported through the system at optimum usable concentrations with minimum loss due to oxidation, reduction, adsorption on corrosion byproducts, adsorption on solids in the system, or reaction with system physical equipment.

Limitations

(a) Results are of little value if there is not a sufficiently accurate method to analyze test samples for low concentrations of corrosion inhibitor.

(b) Test results can be clouded by interference from components in the test samples and can be difficult to overcome.

(c) Unless care is used in securing a representative sample at a given location, the test results can be misleading.

5.2.1 Filming Corrosion Inhibitor Residual

Definition and Scope

Filming corrosion inhibitors are chemical products that are used in low concentrations to adsorb on system surfaces. The adsorbed film of inhibitor shields the system equipment from corrodents in the environment. Inhibitor residual measurements are usually made to ensure that an adequate supply of inhibitor has been introduced into the system to compensate for reduction of concentration by adsorption and maintenance of inhibitor film. This technique is not used on-line or for real-time measurement.

Characteristics of the Technique

(a) Filming corrosion inhibitor residual is measured at one or more locations in a system using acceptable analytical techniques.

(b) Proper sample locations can assure obtaining representative sampling of system fluids.

Benefits

(a) Procedures can be used to measure and ensure that there is adequate transport of a preselected inhibitor throughout a system.

(b) Sudden or unexpected loss of inhibitor due to system changes can be detected and correction in system operation can be effected before significant damage to equipment occurs.

(c) Inhibitor residual measurements can be used to ensure adequate treatment of the system when it is not possible to use direct corrosion-measuring devices, e.g., buried pipelines.

Limitations

(a) Inhibitor residual measurements are only of value if the analytical procedure has been proved to be accurate.

(b) Accurate inhibitor residual measurements are not a direct measure of corrosion protection. Other tools are typically used to select a correct inhibitor and treating dosage.

(c) Proper sample locations help to obtain representative samples of test fluids for analysis.

5.2.2 Reactant Corrosion Inhibitor Residual

Definition and Scope

Reactant corrosion inhibitors are defined as chemicals that react with potential corrodents in a system to neutralize their harmful effect. Further, reactant chemicals can combine with constituents in a system to produce in situ corrosion inhibitors.

Reactant corrosion inhibitor residual measurements are used to ensure that sufficient reactant inhibitor has been injected into the system to provide an excess of reactant. This technique is not used on-line or for real-time measurement.

Characteristics of the Technique

(a) Reactant corrosion inhibitors can be alkaline neutralization chemicals used to maintain a safe operating pH in a portion of a system or total system. For example, neutralization inhibitors can be used to adjust the pH at the point of condensation of acid gases in a distillation system. A typical parameter in determining the effectiveness of such an inhibitor is the ability to measure the control of the pH at the appropriate point in the system.

(b) Reactant inhibitors can be used to react with or reduce oxidants in a system to remove them from the environment. Reactants accomplish their task within the time frame and operating parameters of a system. Measurement of residual reactant inhibitor can be used to indicate whether a decrease of concentration has taken place due to reaction with, and removal of, an unwanted oxidant. Residual measurement can be used to ensure that adequate inhibitor has been introduced into the system to remove oxidants or other corrosive constituents.

Benefits

(a) Reactant corrosion inhibitor residual measurements can be used to ensure that a system has been treated with sufficient inhibitor to adjust pH properly and achieve corrosion protection.

(b) Inhibitor residual measurements can be used to determine whether sufficient inhibitor has been introduced into the system to react with environment constituents to form an in situ inhibitor in some instances.

(c) Inhibitor residuals can be used to determine whether sufficient inhibitor has been used to react with system surfaces to form a protective barrier against corrosion. Reactant chemicals can include chromates, ferrocyanides, sulfur or sulfide compounds, phosphates, acetylenic alcohols, etc. Sufficient reactant inhibitor is used to provide a protective film and leave a residual to repair breaks in the protective barrier.

Limitations

(a) Samples of system fluids cannot always be taken at or near the point of condensation of acid gases to measure effectiveness of neutralization inhibitors.

(b) Measurement of reactant inhibitor used to remove oxidants from a system can be taken after the point of introduction of oxidant (oxygen or air entry, for example) to ensure that sufficient inhibitor has been used to react and leave a residual of inhibitor. This type of inhibitor can include sulfites, bisulfites, and hydrazine as typical examples. The presence of a reducing agent alone cannot be assumed to indicate control of an oxidizing corrodent. Reaction inhibitors, such as catalyst poisons, can prevent desirable reactions from taking place, thereby allowing corrosion to occur.

(c) Sufficient dosage of reactant inhibitor may not have been used in a system and sufficient reaction time/temperature may not have been provided to achieve neutralization, scavenging, and in situ film formation.

5.3 Chemical Analysis of Process Samples

Definition and Scope

Chemical analysis of process samples taken at times of high and low corrosion rates can be useful in identifying the constituents that cause the high corrosion rates. From this information the source of these aggressive constituents can be found and corrected or modified. In petroleum production, crude oil and gas condensate samples are typically analyzed for organic nitrogen and acid. Sulfur, organic acid, nitrogen, and salt content are typically measured for refining purposes. These parameters are used in combination to predict the corrosiveness of the oil. In gas handling and gas processing operations, samples of produced and processed natural gas and gas-liquids are typically analyzed to determine hydrogen sulfide (H_2S), carbon dioxide (CO_2), water (H_2O), carbonyl sulfide (COS), carbon disulfide (CS_2), mercaptans (RSH), and/or oxygen (O_2) to predict and assess corrosion potential in producing wells, gas gathering systems, and gas processing operations. Factors that decrease corrosion upstream (production) are often detrimental downstream (refining). This technique is not used on-line or for real-time measurement.

Other Sources of Pertinent Information

ASTM Section 5. "Petroleum Products, Lubricants, and Fossil Fuels." West Conshohocken, PA: ASTM, 1999.

"Corrosion in the Petrochemical Industry." Ed. L. Gaverick. Materials Park, OH: ASM International, 1994.

Efird, K.D., R.J. Jasinski. "Effect of the Crude Oil on the Corrosion of Steel in Crude Oil/Brine Production." *Corrosion* 45, 2 (1989): p. 65.

Gas Processors Association (GPA)(10) Engineering Data Books, GPA Test Standards, and GPA Sampling Methods. Tulsa, OK: GPA.

Gutzeit, J. "Napthenic Acid Corrosion in Oil Refineries." *Materials Performance* 16, 10 (1977): p. 47.

Piehl, R.L. "Correlation of Corrosion in a Crude Distillation Unit with Chemistry of Crudes." *Corrosion* 16, 6 (June 1960): p. 305t.

White, R.A., and E.F. Ehmke. *Materials Selection for Refineries and Associated Facilities*. Houston, TX: NACE, 1991.

Characteristics of the Technique

(a) In this technique, a representative sample of a process stream is taken and kept in a vessel that maintains the original condition of the sample for subsequent analysis. The techniques for representative sampling are more complicated than may appear initially.

(b) Analysis of the samples under the pressure conditions of the process stream can be critical to maintain the constituents the same as under the operating conditions. This can be particularly difficult for high-pressure process systems.

Benefits

(a) Specific constituents that cause the corrosive conditions can be identified to simplify corrective measures.

(b) Process chemistry can be more accurately understood.

Limitations

Obtaining, storing, and analyzing process samples can be difficult, time-consuming, and expensive.

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(10) Gas Processors Association (GPA), 6529 East 60th St., Tulsa, OK 74145.

5.3.1 Sulfur Content

Definition and Scope

Sulfur is the most abundant element in petroleum other than carbon and hydrogen. It can be present as elemental sulfur, H_2S, mercaptans, sulfides, and polysulfides. The total sulfur content is generally analyzed according to ASTM D 4294.[15] Halides and heavy metals interfere with this method. This technique is not used on-line or for real-time measurement.

Relationship to Corrosion

Corrosion of carbon steel can become excessive when the sulfur exceeds 0.2%.

Benefits

It provides some predictive indication of the corrosiveness that can be expected from the particular process fluid, which in turn can be used to establish operating limits and chemical treatment parameters to control corrosion.

Limitations

(a) The capability of a sulfur compound to form H_2S during heating in the refinery process, rather than the total amount of the compound, is believed to correlate with corrosion in the plants.
(b) A standard procedure for assessment of H_2S evolution is not currently available.

5.3.2 Total Acid Number

Definition and Scope

Acid content is generally expressed in terms of total acid number (TAN) or neutralization (neut) number. An oil sample is dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water. The solution is then titrated with an alcoholic potassium hydroxide solution (KOH). Both ASTM D 664[11] and ASTM D 974[12] can be used to determine the TAN. Inorganic acids, esters, phenolic compounds, sulfur compounds, lactones, resins, salts, and additives such as inhibitors and detergents sometimes interfere with the measurement. UOP(11) Methods 565[13] and 587[14] give procedures to remove most of the interfering materials prior to measuring the organic acids. This technique is not used on-line or for real-time measurement.

Relationship to Corrosion

For the purpose of predicting corrosion in crude distillation units in refineries, the TAN threshold is believed to be around 0.5 for whole crude and 2.0 for the cuts. In petroleum production, it has been found that the higher the algebraic product of the organic nitrogen concentration in weight percent and the TAN, the lower the corrosion rate.

Benefits

It provides some predictive indication of the corrosiveness that can be expected from the particular crude oil when it is processed, which in turn can be used to establish operating limits and chemical treatment parameters to control corrosion.

Limitations

(a) ASTM D 664 yields 30% to 80% higher numbers than ASTM D 974.
(b) For refinery corrosion effects, the TAN can be determined in each distillation cut in order to predict where the acids concentrate during the distillation of the crude.
(c) The assays of the crude, including the organic acid content, can change once steam flooding or another recovery method begins in an oil field. Fire flooding, when used in some fields, tends to increase the acid content.
(d) Correlation of the TAN of the specific cut with its corrosiveness is still not available.

5.3.3 Nitrogen Content

Definition and Scope

The total nitrogen is generally analyzed according to ASTM D 3228.[16] This technique is not used on-line or for real-time measurement.

Relationship to Corrosion

A high nitrogen content indicates corrosion-inhibitive properties of the crude oil or condensate in petroleum production. The higher the algebraic product of the organic nitrogen concentration in weight percent and the TAN, the lower the corrosion rate. In refining, however, when the organic nitrogen concentration exceeds 0.05%, cyanide and ammonia can form, collect in the aqueous phase, and corrode certain materials.

Benefits

It provides some predictive indication of the corrosiveness that can be expected from the particular crude oil when it is processed, which in turn can be used to establish operating limits and chemical treatment parameters for corrosion control.

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(11) UOP, 25 E. Algonquin Rd., Des Plaines, IL 60017-5017.

Limitations

(a) It is limited to crude oil applications.
(b) It is only part of the assessment of the corrosiveness of the process feedstock.

5.3.4 Salt Content of Crude Oil

Definitions and Scope

Salt (primarily sodium chloride with lesser amounts of calcium and magnesium chloride) is present in produced water, and this produced water can be dispersed, entrained, and/or emulsified in crude oil. The salt content of crude oil can be determined using ASTM D 3230.[17] The analytical procedure assumes that calcium and magnesium exist as the chlorides and all the chloride is calculated as sodium chloride. This analysis technique is not used on-line or for real-time measurement.

Relationship to Corrosion

Salt can cause corrosion of refinery equipment and piping by the formation of hydrochloric acid through hydrolysis and heating. Salt precipitates can form scale in heaters and heat exchangers and this can result in accelerated corrosion of equipment. Refineries generally limit salt content of crude oil for processing to 2.5 to 12 mg/L (1 to 5 lb/1,000 bbl).

Benefits

It provides an indication of the corrosiveness of the crude oil to be processed and can be used to establish operating limits plus physical and mechanical treatment parameters for corrosion control.

Limitations

This is only part of the assessment of the corrosiveness of the crude process feedstock.

References

1. ASTM G 31 (latest revision), "Standard Practice for Laboratory Immersion Corrosion Testing of Metals" (West Conshohocken, PA: ASTM).

2. ASTM G 96 (latest revision), "Standard Guide for On-Line Monitoring of Corrosion in Plant Equipment (Electrical and Electrochemical Methods)" (West Conshohocken, PA: ASTM).

3. ASTM G 102 (latest revision), "Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements" (West Conshohocken, PA: ASTM).

4. ASTM G 5 (latest revision), "Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements" (West Conshohocken, PA: ASTM).

5. ANSI/ASME B31G (latest revision), "Manual for Determining the Remaining Strength of Corroded Pipelines" (New York, NY: ANSI/ASME).

6. API Standard 653 (latest revision), "Tank Inspection, Repair, Alteration, and Reconstruction" (New York, NY: API).

7. API Standard 510 (latest revision), "Pressure Vessel Inspection Code: Maintenance Inspection, Rating, Repair, and Alteration" (New York, NY: API).

8. ASME Boiler & Pressure Vessel Code, Section VIII, Division 1 (latest revision), "Rules for Construction of Pressure Vessels" (New York, NY: ASME).

9. API RP 941 (latest revision), "Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants" (Washington, DC: API).

10. API RP 14E (latest revision), "Recommended Practice for Design and Installation of Offshore Production Platform Piping Systems" (Washington, DC: API).

11. ASTM D 664 (latest revision), "Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration" (West Conshohocken, PA: ASTM).

12. ASTM D 974 (latest revision), "Standard Test Method for Acid and Base Number by Color-Indicator Titration" (West Conshohocken, PA: ASTM).

13. UOP Method 565 (latest revision), "Acid Number and Naphthenic Acids Potentiometric Titration" (Des Plaines, IL: UOP).

14. UOP Method 587 (latest revision), "Acid Number and Naphthenic Acids by Colorimetric Titration" (Des Plaines, IL: UOP).

15. ASTM D 4294 (latest revision), "Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy-Dispersive X-ray Fluorescence Spectroscopy" (West Conshohocken, PA: ASTM).

16. ASTM D 3228 (latest revision), "Standard Test Method for Total Nitrogen in Lubricating Oils and Fuel Oils by Modified Kjeldahl Method" (West Conshohocken, PA: ASTM).

17. ASTM D 3230 (latest revision), "Standard Test Method for Salts in Crude Oil (Electrometric Method)" (West Conshohocken, PA: ASTM).