

# **Improving Plant Reliability Through Corrosion Monitoring**

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# Improving Plant Reliability Through Corrosion Monitoring

## Abstract

Corrosion is major problem in petroleum refineries and chemical process plants. Key equipment, such as piping, valves, vessels, vessel internals, condensers, boilers, and heat exchangers, can be degraded by corrosion attack. Such attack can reduce equipment performance and reliability and, in extreme cases, lead to unexpected failures and shutdowns. Typically, indications of corrosion are found by means of inspections conducted during planned shutdowns and preventative maintenance. If corrosion has been unexpectedly severe or if inspections have been infrequent, equipment damage can occur. Corrosion monitoring during operation can help minimize such damage by indicating when corrosion initiated and by measuring the rate of corrosion damage. This information then can be used to alter operating conditions to reduce corrosion or to plan maintenance and repair work.

This paper reviews the features, advantages, and disadvantages of both established and emerging technologies for corrosion monitoring. Established technologies include measuring environmental conditions, exposing material coupons, and using electrical resistance, linear polarization resistance, and galvanic probes. Emerging technologies include the use of advanced electrochemical testing techniques and the application of specialized probes for stress-corrosion cracking and pitting corrosion. Examples that illustrate the use of both established and emerging corrosion monitoring technologies are presented and discussed.

## Introduction

Much of the key equipment used in petroleum refineries and chemical process plants has been in service for a long time, often 10 years or more. As this equipment grows older, the materials from which it is made are subject to aging. Corrosion attack is the most serious aging mechanism for such equipment, especially for vessels, piping, valves, and pressure-boundary components that contain hazardous fluids. Corrosion can cause either a penetration of the fluid containment boundary that results in leak or a decrease in structural strength that results in a component failure. For the safe and reliable operation of these components, it is important to detect and quantify the amount of corrosion that occurs.

Corrosion attack of process equipment may be external or internal. External attack is caused by the corrosive species in the ambient environment, whereas internal attack is caused by fluids being transported, stored, or processed. In a general corrosion assessment, the possibility of both external and internal attack must be considered. Corrosion can limit the safe and useful life of process equipment. Thus, the effects of corrosion must be incorporated into component remaining life assessment and aging management programs.<sup>1-5</sup> Corrosion monitoring is an essential element of these programs and is used to assess the deterioration of structural and mechanical components.<sup>6</sup> Corrosion monitoring also can provide significant benefits when it is integrated into process control.<sup>7,8</sup>

## Background

Corrosion monitoring has been utilized for many years and has evolved into a relatively sophisticated field of technology. In the past, the oil and gas industry has employed corrosion monitoring more than other industries<sup>9-13</sup>. The chemical process industry also has used corrosion monitoring methods for a number of years<sup>14</sup>, and other industries have begun to use corrosion monitoring to evaluate the performance and reliable life of equipment.<sup>15,16</sup>

Corrosion monitoring techniques can be divided into (1) methods that indirectly measure parameters related to corrosion and then infer corrosion behavior from some model of the corrosion process and (2) methods that directly measure corrosion behavior. Table 1 summarizes the primary corrosion monitoring techniques in these two categories. The indirect techniques use parameters that indicate the presence or absence of corrosion and/or the degree of corrosion in specific material/environment system. For example, electrochemical potential, pH, and temperature are commonly measured for this purpose. The primary purpose of this paper is to review direct measurement techniques, which is the focus of the remaining discussion.

*Table 1. Summary of Corrosion Monitoring Techniques.*

<b>Direct Measurement</b>	<b>Indirect Measurement</b>
Nondestructive Inspection (NDI)	Biological Counts
Material Test Coupons	Potential*
Cyclic Potentiodynamic Polarization (CPP)	Hydrogen*
Electrical Resistance (ER) Probes	Specific Ions*
Linear Polarization Resistance (LPR)*	pH*
Galvanic Currents (GC)*	Temperature*
Electrochemical Impedance Spectroscopy (EIS)*	Conductivity*
Electrochemical Noise (EN)*	

\* Capable of continuous monitoring.

The asterisks in Table 1 indicate techniques that can be used to continuously monitor corrosion, whereas the other techniques are applicable to only periodic monitoring. Continuous monitoring techniques also can be applied periodically. No direct measure of corrosion rate is truly continuous. There is always some time interval required to collect and analyze the data that are used for calculation of the corrosion rate. However, when measurements can be made in a relatively short time interval with respect to process fluctuations, they are considered to be continuous, as is indicated in Table 1.

Periodic assessment is the most common and widely used method of corrosion monitoring. The main reasons for performing periodic monitoring are (1) to evaluate materials performance under service conditions, (2) to aid in materials selection, (3) to evaluate and control the production process, and (4) to provide information for life assessment. The main reasons for performing continuous monitoring are (1) to provide integrated process control, (2) to continuously evaluate materials performance, and (3) to measure parameters used in on-line life assessment. The

emphasis of this paper is on continuous monitoring techniques. Techniques that are restricted to periodic monitoring will be discussed only briefly.

### **Established Corrosion Monitoring Methods**

Nondestructive inspection (NDI), material coupon exposures, cyclic potentiodynamic polarization (CPP), electrical resistance (ER), linear polarization resistance (LPR), and galvanic-current (GC) measurement are well established techniques for corrosion monitoring. Each of these techniques is discussed separately in the following sub-sections of this paper.

#### **Nondestructive Inspection (NDI)**

NDI is the most widely used method of periodic corrosion monitoring. Magnetic flux leakage (MFL), ultrasonic testing (UT), radiography, calipers, and depth gauges are used to measure wall thickness. Trends in the amount of wall loss and the general corrosion rate can be established from measurements taken at the same location at various times in the operating history of a component.

MFL can cover large areas in a relatively short time and provides a rapid, economic means of detecting and characterizing areas of significant wall loss. For example, MFL is used to inspect storage tanks and underground pipelines. However, MFL can be applied only to ferrous materials, is not as sensitive to local variations in wall thickness as other methods, and cannot be used to inspect welds.

UT is widely used to measure wall thickness and to detect and characterize cracks. UT is applicable to all structural metals and alloys. With appropriate calibration standards, proper transducers, and modern, computerized instrumentation, UT can be employed to inspect regions near welds. UT is typically more sensitive than MFL, but coverage of large areas requires much longer inspection times with UT than with MFL.

Radiography is used in certain limited cases to measure wall thickness and detect cracks. Calipers and depth gauges also find limited application. They can be used to measure wall thickness or depth of corrosion attack only when there is sufficient access to the area that is to be inspected.

#### **Material Coupon Exposures**

Unstressed material coupons are often exposed to the operating environment to periodically evaluate corrosion behavior. After some planned exposure time, the coupons are removed from the environment, examined for evidence of localized corrosion attack such as pitting or cracking, and weighed to determine the amount of material lost during the exposure period. The corrosion rate, CR, ( $\mu\text{m}/\text{year}$ ) is then determined using the following relationship:

$$\text{CR} = \frac{10,000\text{WL}}{\text{D A t}} \quad (1)$$

where WL is the coupon weight loss (g), D is the material density ( $\text{g/cm}^3$ ), A is the exposed surface area of the coupon ( $\text{cm}^2$ ), and t is the exposure time (year). If localized attack is observed, the depth of attack is obtained from surface measurements or from measurements on metallographic sections through the coupon.

Stressed specimens are sometimes exposed to the operating environment to assess a material's susceptibility to stress-corrosion cracking. Pre-stressed U-bend specimens or bolt-loaded three-point bending specimens are used to evaluate stress-corrosion-crack initiation resistance. Wedge-opening-loading (WOL) type compact tension specimens are used to measure stress-corrosion-crack growth behavior and to evaluate the threshold stress intensity factor for stress-corrosion cracking.

### **Cyclic Potentiodynamic Polarization (CPP)**

To a limited extent, CPP tests have been used in the field.<sup>7,17</sup> However, CPP is an electrochemical technique that is primarily used in the laboratory to evaluate the possibility for initiation of pitting and crevice corrosion. With this technique, a metal sample is immersed in an actual or simulated electrolyte, the electrochemical potential is scanned with respect to a reference electrode, and the ensuing current is measured. Details of the CPP technique are given in ASTM-G-61. CPP is an accelerated, destructive testing technique. For field use, the CPP probe typically must be replaced after each test, which makes CPP testing a periodic corrosion monitoring technique.

### **Electrical Resistance (ER)**

The ER method can be applied to a broad range of corrosion conditions, including environments consisting of poor or non-continuous electrolytes, such as vapors, gases, "wet" hydrocarbons, and non-aqueous liquids. This method is based upon the simple measurement of the electrical resistance of a metal probe (or element) exposed to the service environment. The probe resistance, R, is given by the following expression:

$$R = \rho \left( \frac{L}{A} \right) \quad (2)$$

where  $\rho$  is the resistivity of the probe material, L is the probe length, and A is the probe cross-sectional area. Corrosion causes a reduction of A, which is accompanied by a corresponding proportional increase in R, based on Equation (2). Since a fairly long time is usually required to produce a significant change in R, ER is a periodic corrosion monitoring technique.

Practical ER probe designs include an embedded reference element that does not corrode. The reference element is used to compensate for temperature variations since it is maintained at the same temperature as the exposed element. A wide variety of probe configurations are commercially available. These can be applied to most corrosion monitoring applications in the process industry. Its general applicability and relatively low cost make the ER technique quite popular for general industrial use.

The industrial use of ER monitoring is quite varied. Example applications include fluidized bed combustors, components exposed to the atmosphere, oil field equipment, and chemical process equipment.<sup>18-24</sup> Gareau<sup>23</sup> illustrated the use of a computerized system for data transmission from several remote sites to a central control facility. At this central facility, the ER data were

monitored in real time, manipulated, and analyzed to obtain information on corrosion at the remote sites.

Thierry, et al.<sup>25</sup> compared the results of weight-loss-coupon exposures, ER measurements, and linear polarization resistance (LPR) measurements (see next sub-section of this paper) in cooling water systems. They concluded that the ER measurements indicated corrosion rates greater than those observed on the coupons when there was significant localized corrosion of the coupons. These results point out that the ER technique is sensitive to pitting attack and provides a rate that is some intermediate value between the general corrosion rate and the penetration rate. However, the exact relationship between the measured rate and the actual rates is unknown. Thierry, et al.<sup>25</sup> also found that the LPR technique could detect sudden changes in the corrosivity of the water within a few hours, whereas the ER technique took several days to detect these changes in corrosivity. This result experimentally confirms that ER is a periodic corrosion monitoring technique.

### Linear Polarization Resistance (LPR)

LPR is the most common continuous monitoring technique employed to determine corrosion rate. Figure 1 schematically illustrates an analog electrical circuit for a simple corroding fluid/metal interface. The solution resistance ( $R_s$ ) is the resistance between the corroding interface and the reference electrode used to perform the electrochemical measurement. The polarization resistance ( $R_p$ ) is related to the corrosion rate. When a DC or low-frequency AC corrosion rate measurement is made,  $R_s$  and  $R_p$  are two resistors in series. The resistivity of many aqueous environments is relatively low. In these cases,  $R_s$  is often negligible compared with  $R_p$  and can be ignored in calculating the corrosion rate. However, in some aqueous environments, atmospheric environments, soils, and concrete,  $R_p$  must be measured separately from  $R_s$  to avoid errors in calculating the corrosion rate.

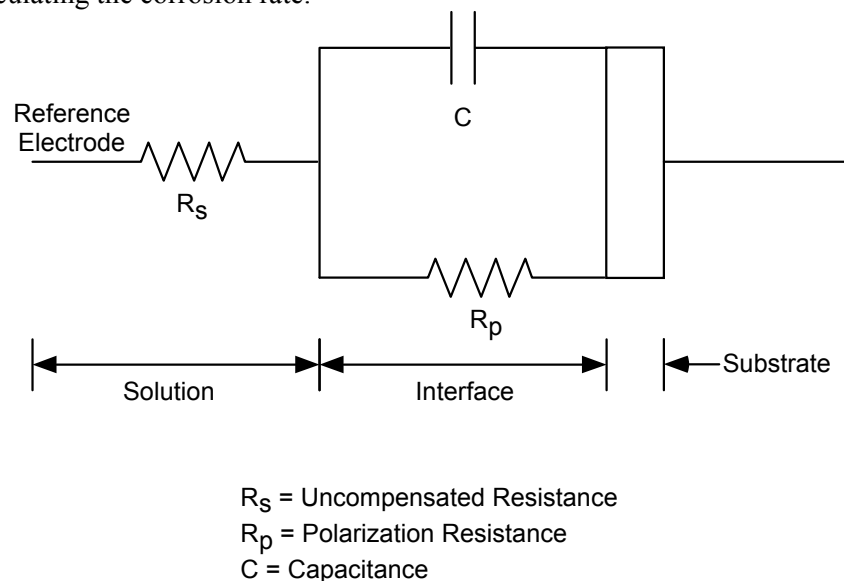


Figure 1. Analog Circuit for a Single Time Constant Corroding Interface.

For small changes ( $\pm 20$  mV) from the free-corrosion potential, Stern and Geary<sup>26</sup> showed that the relationship between  $R_p$  and corrosion rate was well approximated by the following equation:

$$R_p = \frac{\Delta E}{\Delta I} = \frac{\beta_a \beta_c}{2.3 I_{cor} (\beta_a + \beta_c)} \quad (3)$$

where  $\Delta E$  is the change in corrosion potential,  $\Delta I$  is the change in corrosion current,  $I_{cor}$  is the corrosion current density,  $\beta_a$  is the anodic Tafel slope, and  $\beta_c$  is the cathodic Tafel slope. Equation (3), known as the Stern-Geary equation, shows that  $R_p$  is the slope of the linear E versus I relationship near the free-corrosion potential. The Tafel slopes are estimated as the magnitude of the change in potential per decade of current as the potential is shifted away from the free-corrosion potential in the anodic or cathodic direction.  $\beta_a$  is the anodic Tafel slope, while  $\beta_c$  is the cathodic Tafel slope. If a proportionality constant, C, is defined as

$$C = \frac{\beta_a \beta_c}{2.3 (\beta_a + \beta_c)} \quad (4)$$

then, from Equation (3), it follows that

$$I_{cor} = \frac{C}{R_p} \quad (5)$$

The corrosion rate (CR) can be computed from  $I_{cor}$  using the following equation:

$$CR = \frac{I_{cor} M}{F Z D} \quad (6)$$

where M is the molecular weight of the metal, F is Faraday's constant, Z is the metal's valence, and D is the metal's density.

To apply the LPR technique, the potential is varied 20 mV or less above and below the free-corrosion potential and the corresponding current is measured. Figure 2 shows an example of such LPR data. The plotted symbols connected by the light line represent the actual measured data, while the heavy line represents the best linear fit of the data. The slope of this line is the value of  $R_p$ . In typical applications of the LPR technique, automated instrumentation is used to obtain the data and compute  $R_p$ , and a correction is made for the value of  $R_s$  in high resistivity environments.<sup>27</sup>

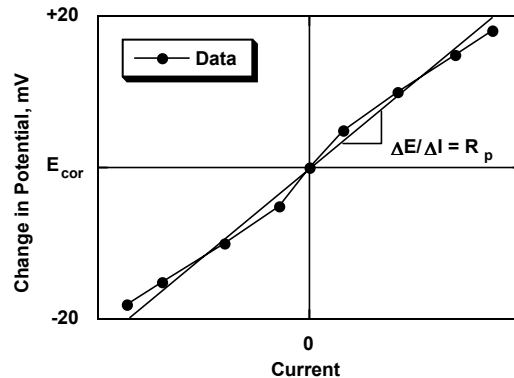


Figure 2. Typical Potentiodynamic Linear Polarization Resistance (LPR) Data.

The LPR technique is widely used by industry to continuously monitor corrosion rates. In the past, the use of LPR measurements was limited to aqueous solutions with low resistivities. In recent years, special probes have been developed for high-resistivity and atmospheric environments,<sup>28-30</sup> and the use of atmospheric LPR probes has become commonplace.<sup>31</sup> Figure 3 illustrates typical commercially available LPR probe configurations. The triangular and linear configurations have three elements that protrude into the environment, whereas the flush configuration has three concentric elements that are mounted flush with the wall of the equipment. Applications of LPR include oil-field equipment,<sup>32,34</sup> pipelines,<sup>35-36</sup> chemical process plants,<sup>37,38</sup> pulp and paper plants,<sup>39</sup> and water treatment equipment.<sup>40</sup>

### **Galvanic-Current (GC) Measurement**

Galvanic-current measurements are used to monitor corrosion rates in cooling water systems. The galvanic probe contains elements of two dissimilar metals, and the galvanic current between them is measured using a zero-resistance ammeter. This current is then correlated with the corrosion rate of the more active of the two metals in the probe.<sup>41,42</sup> GC measurements are used to monitor water injection systems or other water-system equipment where oxygen leaking into the water can markedly increase the corrosion rates of steel components. Increased levels of dissolved oxygen in the water greatly increase the galvanic currents and are correlated with corrosion rates.

## **Emerging Corrosion Monitoring Methods**

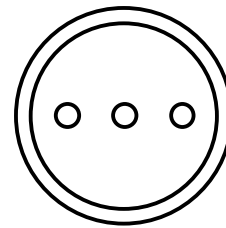
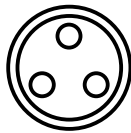
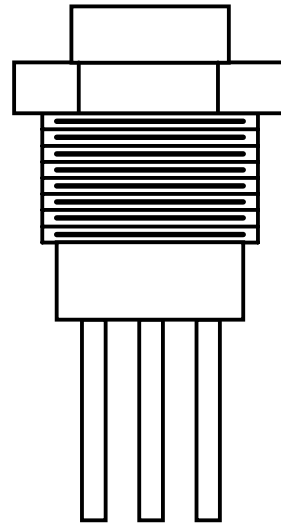
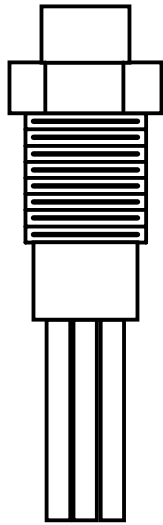
Electrochemical noise (EN), electrochemical impedance spectroscopy (EIS), and special-purpose probes are emerging techniques for corrosion monitoring. Each of these techniques is discussed separately in the following sub-sections of this paper.

### **Electrochemical Noise (EN)**

Several investigators<sup>43-49</sup> have reviewed the application of EN measurement to corrosion monitoring. This technique utilizes measurements of transient electrochemical events, typically in the range of  $10^{-3}$  to 1 Hz, that are produced by the corrosion process. One or both of the following two types of transient measurements are normally made: (1) the potential noise between two identical electrodes and/or (2) the current noise between two identical electrodes coupled through a zero-resistance ammeter.

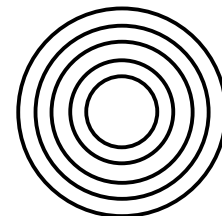
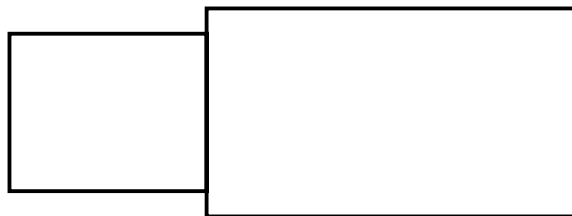
The measured data are analyzed to provide information on the type of corrosion, the initiation of localized corrosion, and in some cases, the amount of metal loss. Metal loss is estimated employing a noise resistance value, which is related to the previously described  $R_p$  value. A major advantage of the EN technique is its ability to provide information on localized corrosion — pitting, crevice corrosion, and possibly stress-corrosion cracking. EN is sensitive to pitting corrosion because passive conditions typically generate low noise, whereas unstable or stable pitting generate random events of short duration or individual events of longer duration, respectively. EN monitoring also has been applied to general corrosion,<sup>50-51</sup> stress-corrosion cracking,<sup>50-54</sup> and corrosion of coated metals.<sup>55,56</sup>

The EN technique is considered to provide continuous monitoring for practical applications. Like other electrochemical methods, EN results are based on analysis of data collected over



**Triangular Configuration**

**Linear Configuration**



**Flush Configuration**

*Figure 3. Illustration of Typical Linear Polarization Resistance (LPR) Probes.*

some time period ranging up to several minutes. Limitations of this method are that it requires (1) relatively expensive equipment, (2) sophisticated analysis and expert interpretation of the data, and (3) minimization or filtering of background electrical noise that can mask EN in the field. The industrial use of EN monitoring should increase as these limitations are overcome by future developments.

### Electrochemical Impedance Spectroscopy (EIS)

EIS is a continuous corrosion monitoring method similar to LPR. Instead of employing a DC potential, as does LPR, EIS employs a variable-frequency AC excitation potential. EIS measures the same  $R_p$  value as LPR method, and that value is related to corrosion rate by Equations (3) through (6). LPR determines only  $R_p$ , whereas EIS determines both  $R_p$  and  $R_s$ , as well as providing mechanistic information. If the  $R_s$  value is not significant or if the LPR instrumentation corrects for the  $R_s$  error, EIS has little advantage over LPR as a continuous corrosion monitoring technique.

EIS is typically implemented by applying a series of sinusoidal potential fluctuations at amplitudes of  $\pm 10$  to 15 mV about the free-corrosion potential and at frequencies in the range of  $10^{-3}$  Hz to 20 kHz. The current waveform is measured for each applied potential waveform. Impedance is then calculated by dividing the applied potential by the corresponding measured current, and a Bode plot of the logarithm of impedance as a function of the logarithm of frequency is prepared as shown in Figure 4. Assuming a single time constant circuit analog model (Figure 1), the high-frequency impedance represents  $R_s$  and the low-frequency impedance represents  $R_p + R_s$ . The value of  $R_p$  is calculated by subtracting the high-frequency impedance from the low-frequency impedance. The low-frequency EIS measurement is equivalent to the LPR measurement, in that both yield the value of  $R_p + R_s$ .

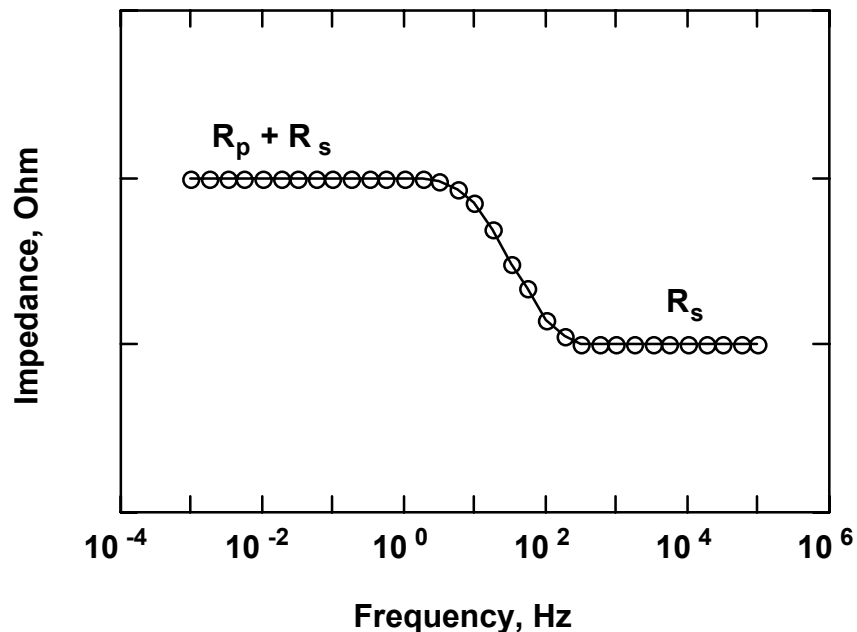


Figure 4. Typical Bode Plot Produced by EIS Measurements.

Several reviews of corrosion monitoring techniques include discussions of EIS.<sup>57-60</sup> EIS techniques are not generally used in industrial corrosion rate monitoring systems because of the higher equipment cost and increased data analysis required by EIS compared with LPR. However, EIS has been used to periodically assess corrosion rates for many industrial components,<sup>61</sup> reinforcing steel in concrete,<sup>28,62,63</sup> high-temperature equipment,<sup>64,65</sup> underwater pipelines,<sup>66</sup> sour gas equipment,<sup>67</sup> and organic coatings on metal.<sup>68,69</sup>

### **Special-Purpose Probes**

Most of the commercial techniques for corrosion monitoring described above measure rates of general corrosion and are relatively insensitive to localized forms of corrosion. Techniques such as ER and LPR measure average properties and are inherently insensitive to localized phenomenon, such as pitting and stress-corrosion cracking. The EN technique is capable of indicating the initiation of localized corrosion but generally does not provide corrosion-rate information. The general applicability of EN to monitoring stress-corrosion cracking also has not been established.

Because of the shortcomings of the current techniques, there is considerable interest in developing simple, direct techniques for monitoring localized corrosion. CC Technologies recently applied for a patent on a probe for monitoring stress-corrosion cracking (Application Number 08/418,015). The probe consists of a pressurized tube that is inserted into the process stream or operating environment. The applied pressure is adjusted to provide the desired stress in the tube wall and monitored to indicate when failure occurs. The tube material is selected to simulate that used in the equipment that is being monitored. Alternatively, the probe material can be modified to provide an acceleration of the localized corrosion attack. For example, a sensitized stainless steel probe can be used to simulate worst-case conditions for a stainless steel vessel. The internal pressure within the probe can be varied to accelerate or decelerate the rate of attack and to give a means of discriminating among the mechanisms of attack. These stress-corrosion cracking probes show promise and currently are being evaluated by means of both laboratory and field testing.

### **Discussion and Summary**

Corrosion monitoring instrumentation and methodologies are becoming more sophisticated and reliable. Established methods that monitor general corrosion continue to be improved and refined. Emerging methods for monitoring localized corrosion are being developed and field testing. Both periodic and continuous monitoring techniques are available for industrial application. Periodic techniques are relatively inexpensive and fairly easy to incorporate into plant maintenance programs. Periodic monitoring can provide valuable information on long-term trends in material degradation, but there is a chance for significant corrosion attack to occur between measurements. In contrast, continuous monitoring allows corrosion conditions to be measured in real time, so sudden changes in corrosion conditions can be detected and dealt with in a timely fashion.

Nondestructive inspection for corrosion attack should be included in all equipment reliability management and maintenance programs. Additional periodic corrosion data can be obtained by use of material coupon exposures and ER probes. The LPR technique can be employed to continuously monitor general corrosion behavior. Emerging techniques, such as EN and EIS, can provide information on localized corrosion and corrosion mechanisms. Special probes for

monitoring pitting and stress-corrosion cracking are valuable tools for monitoring localized corrosion.

Indirect methods also can be employed to monitor corrosion in process-plant equipment. Important parameters to measure include potential, pH, temperature, conductivity, and hydrogen permeation. These parameters can be controlled within predetermined limits to minimize corrosion attack. If a suitable model of the corrosion process is available, a formulation of the model can be incorporated into a computer system along with feedback signals from transducers that measure the indirect parameter. The computer system then can compute estimates of corrosion behavior in real time.

Corrosion monitoring should be an essential element of plant-reliability programs. Systematic procedures for corrosion monitoring provide a cost-effective means of improving the reliability of important components and equipment that are potentially subject to degradation from corrosion. Traditional periodic monitoring techniques are typically part of plant maintenance and in-service inspection programs. These periodic methods are economic to use but they do not provide rapid feedback on changes or upsets in the environment or manufacturing process that may significantly affect the integrity and reliability of operating equipment. Continuous monitoring techniques do provide rapid feedback on changes in the environment or manufacturing process, which allows plant operators to address potential problems in timely manner and avoid costly unscheduled shutdowns for repairs and replacements.

Corrosion monitoring can be used to monitor process conditions. The effects of proposed changes in operating conditions on key plants components can be evaluated by using corrosion monitoring during trial runs. The results of such monitoring can then be used to modify proposed operational changes or to employ alternate materials in areas that are subject to unacceptably high corrosion attack. Corrosion monitoring also provides an effective means of process control. Information from continuous monitoring can indicate when process parameters are outside of the target range.

Historically, the monitoring methods have been widely applied to general corrosion problems. Thus, economic instrumentation and techniques for general corrosion monitoring are well-established, commercially available, and readily applicable to process-plant equipment. However, many major corrosion problems are caused by localized attack, such as pitting, crevice corrosion, and stress-corrosion cracking, rather than by general corrosion. For this reason, new monitoring methods for sensing localized corrosion are emerging. These emerging methods often employ more costly instrumentation and more complicated analytical procedures than the established methods, but with continued research and development, their industrial use should increase and eventually become widespread.

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