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TAKE CORROSION MONITORING ON-LINE

Treating corrosion as a real-time process variable can play an important part in optimizing plant operations

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The purpose of corrosion monitoring has changed dramatically from the early days of weight-loss-coupon exposure. As new technologies have evolved, the accuracy of data and the relevance of the information to process control have improved. However, many process managers and corrosion engineers still don't appreciate the benefits of on-line, real-time technologies for optimizing processes, reducing downtime and saving plant assets. So, in this article, we will describe the capabilities and application of such monitoring methods.

To set the stage, let's first look at the problem of corrosion. In the real world, corrosion rarely takes place at a steady rate for prolonged periods. Instead there usually are some short periods of very aggressive attack and relatively long periods of little or no attack depending upon process conditions. For example, if the corrosion processes occur for 10% of the time, the actual corrosion rate instead of being, say, 10 mils/yr may peak at ~100 mils/yr or even much higher. These periods of high corrosion rate often go unnoticed until the underlying causes increase in frequency and ultimately lead to failure.

Generally, if a metallic material can corrode then its corrosion behavior can be measured or monitored. Corrosion monitoring techniques are applicable to virtually all metallic materials including, for example: carbon, stainless, duplex and super duplex steels; copper and nickel alloys; titanium and zirconium.

Corrosion damage identified by monitoring or inspection after incurring substantial damage has only limited benefit. The plant engineer or process control specialist can get far more value from data on general and localized corrosion made available on-line and in real-time. The ability to overlay corrosion data with plant or process variables real-time before substantial damage has occurred

effectively takes corrosion to the higher level of being "another process variable." This, then, affords the opportunity to correlate corrosion activity with changes in other process variables and facilitates early mitigation.

For operators, such real-time data can provide an immediate indication of the effect of process changes on corrosion activity and enable rapid adjustments in process conditions or injection of inhibitive chemicals. For engineers, accumulated data can play a crucial role in achieving optimum production rates while protecting plant integrity, e.g., minimizing downtime for repair of damage and increasing equipment service life.

Why, where and how?

Although all monitoring techniques can be applied successfully for almost all metallic materials, the type of corrosion really determines the most appropriate technique. So, it is important to consider three key questions:

Why is corrosion information needed? Sure, you want to find out what is causing the corrosion and reduce or prevent it. However, a deeper consideration of corrosion and its consequences generally will help you to work out your measurement needs such as the frequency of measurement required and the level of corrosion detail necessary. Some thoughts may include:

- Corrosion led to an unplanned shutdown. We need to understand what in the process or unit operation caused the corrosion.
- Some piping was replaced last turnaround but the new piping has corroded through. We want to figure out what to replace it with next time.

- We found some pitting corrosion last inspection but don't know if it was caused by a process upset or something else.
- Our equipment is halfway through its planned design life but we still have 75% of our corrosion allowance left. We need to monitor to check that we really can extend the equipment lifetime reliably.
- We are designing a new process and want to ensure we have selected the correct materials.

Where should corrosion be measured? For an existing plant with a history of inspection and maintenance data, the location of the corrosion probes usually can be worked out easily. However, the determination can become complicated if an existing probe access port is not available. For a new plant, it is wise to consult with a corrosion or materials engineer who can advise on optimal probe locations.



Figure 1. Such coupons continue to play an important role in off-line, retrospective analysis of corrosion.

Source: Metal Samples

While comprehensive monitoring certainly is useful, it is important to consider cost efficiency and ensure that the corrosion measurement in itself will deliver value rather than represent a cost sink.

How should corrosion be measured? Corrosion monitoring methods fall into two distinct groups: cumulative loss techniques (off-line, retrospective) that provide indications of the cumulative damage sustained and corrosion rate techniques (usually on-line and continuous) that provide indications of the prevailing corrosion rate. Reference 1 provides guidance on coming up with a shortlist of candidate techniques and sensors.

Cumulative loss techniques

These methods will only show some signs of change when sufficient metal loss due to corrosion has been sustained. As such, most are used off-line and do not provide real-time data. The techniques include: weight loss coupons, electrical resistance (ER), thin layer activation (TLA), field signature method (FSM), ultrasonic thickness (UT) measurement and other non-destructive examination methods, e.g., radiography. The most popular of these off-line measurements for field corrosion evaluation are:

Weight loss coupon. This is the most widely used method of corrosion evaluation. A metal coupon of known alloy grade, size, shape and weight is exposed to an environment for a set period of time, typically up to three months. Figure 1 shows examples of coupons. At the end of the exposure period, the coupon undergoes removal, visual and optical examination, analysis of corrosion products and measurement of weight loss due to corrosion. The accuracy of this technique typically is limited to about ± 0.1 mg by the weighing process.

Electrical resistance. This measurement can be considered as almost an electronic or instrumented coupon. As the probe “element” corrodes and its thickness decreases, its electrical resistance changes

and this can be converted to a cumulative metal loss value. In many cases, this makes ER measurement an after-the-fact determination of corrosion damage not a real-time control parameter. One of the major benefits of ER is that it works in both conductive and non-conductive environments. However, the measurement is affected by temperature. This means a temperature compensation must be included and may also rule out ER at high or fluctuating temperatures. Figure 2 shows a selection of ER probes.

For conventional ER, the sensitivity of measurement typically is 0.1% of the element thickness (similar limitations apply to TLA, FSM and UT techniques). Such methods are most appropriate where the corrosion rate is relatively stationary, i.e., the rate does not suffer from large excursions. They are useful as accounting tools to provide an indication of the cumulative wastage of a plant asset and, hence, the likely remaining usable life. Overall, the techniques are relatively insensitive to localized corrosion.

Corrosion rate techniques

The most common method is linear polarization resistance (LPR), but recently this has been coupled with newer techniques such as harmonic distortion analysis (HDA) and electrochemical noise (ECN) for greater accuracy and reliability. These techniques have a much higher resolution and faster response than cumulative loss methods. They measure the current produced by corrosion and therefore provide an indication of the electrochemical rate processes taking place at the metal/environment interface. Measurements may take only a few minutes. Some instruments rely on a single measurement method while others, such as SmartCET (Figure 3), use the combination of these techniques that are applied continuously in an automated data acquisition and analysis cycle.

Electrochemical monitoring methods determine the corrosion current. This occurs as a consequence of the corrosion process and its value directly relates to the rate of the metal loss. If the corrosion process is relatively stationary, i.e., at a steady state, then the relationship between the polarization resistance and the corrosion current is given by the Stern-Geary relationship:

$$i_{corr} = B/R_p$$

where R_p is the polarization resistance, B is the Stern-Geary constant and i_{corr} is the corrosion current. (The Stern-Geary constant is a *system* constant, not an instrument or universal constant as often described.)

This is the basis for the use of LPR to estimate general corrosion rates. In the case of the LPR measurement, the polarization resistance is a simple function of the applied voltage and the current response at low frequency. In another, less utilized technique, electrochemical impedance spectroscopy (EIS) is used to determine the characteristic impedance of the corroding metal, typically over the frequency range 1 mHz to 100 kHz. The time this takes usually precludes EIS' use for plant monitoring and process control applications.

HDA, which is a newer approach, also relies on a steady-state approximation but requires more mathematical treatment than necessary for LPR. However, this can all be handled by remote micro-processors and existing computer control systems.

HDA provides values for the corrosion current, the characteristic anodic and cathodic corrosion coefficients and, most importantly and unlike virtually all other corrosion techniques, a value for the Stern-Geary constant. This B value is essential for quantitative corrosion-rate assessment. So, HDA must be used for accurate assessment of damage for applications where process control and asset management are involved.

LPR and HDA are powerful techniques for plant monitoring. While they were developed originally for short-term laboratory evaluation of metallic corrosion, they now are finding increased use in field applications for the determination of general corrosion-rate behavior.

ECN was initially developed to fill a huge gap left by the more conventional techniques, particularly the area of identifying when localized corrosion phenomena, such as pitting, crevice corrosion, stress corrosion cracking, etc., are occurring. A steady-state analogy for these phenomena is not applicable because the localized attack takes place in a discontinuous manner. ECN is used proactively to

identify periods when the corrosion processes become unstable and to recognize when the probability of localized corrosion is high. It differs from LPR in that no applied electrical perturbation of the electrodes is required. The technique measures small naturally occurring variations in current (current noise, typically microamps) and potential (potential noise, typically millivolts). When general corrosion takes place, the potential and current fluctuations can be processed to provide a general corrosion rate using a data treatment similar to that for LPR. However, the more important aspect of ECN monitoring is to spot when localized corrosion phenomena occur. The characteristics of the fluctuations change dramatically during localized corrosion and these characteristics can be used to identify the onset of pitting attack. From a plant corrosion-control perspective, this is important because the technique provides an early real-time warning of incipient localized corrosion before substantial damage has occurred that can be correlated to process or operational events to prompt remedial action.

Localized corrosion

ECN has been widely applied to the evaluation of localized corrosion phenomena, such as pitting, crevice corrosion, environmentally assisted cracking, microbiologically influenced corrosion, etc. Localized corrosion can occur on many metals. In fact, surveys have shown that some 70-90% of all corrosion failures are due to localized corrosion which cannot be monitored with other techniques. Localized corrosion is more insidious than general corrosion because only a small area of the metal is undergoing metal loss and the localized corrosion rate may be one or two orders of magnitude greater than the general corrosion rate.

General and localized corrosion differ in the distribution of anodic and cathodic sites on the metal surface. In the case of general corrosion, the distribution is quite even. Localized corrosion results from situations where a local anodic area can be supported by a relatively large cathodic area — such as where protective film on the metal surface breaks down in a spot, where scale has partially formed or where a local coating holiday occurs. Localized corrosion often appears as pinholes in the metal and potentially can be catastrophic, e.g., in the case of pressurized systems where it can lead to leakage of toxic materials, ignition of flammables and even explosive failure of equipment.

It is important to note that the electrochemical evaluation of localized corrosion usually is limited to identification of high-probability pitting events, as opposed to the rate information available for general corrosion attack. This is because it can be difficult to assess the number, size and distribution of pits or cracks. Accordingly, a pitting probability or “Pitting Factor” provides an easily understood representation of localization or general corrosion. A low value, close to 0, represents general corrosion while a high value, closer to 1, indicates that localized corrosion is occurring. Based both on field experience and laboratory tests, this Pitting Factor scale has been subdivided to include regions for general corrosion, potential risk of pitting, and high pitting tendency.

Localized corrosion monitoring offers significant value by quickly alerting an operator to a condition that, if prolonged, will result in corrosion. This can enable action to be taken *before* substantial damage has occurred.

Extensive study of ECN field data gathered over more than twenty years has led to development of statistical methods to further quantify and differentiate various mechanisms of corrosion. Reference 2 contains information about such data appraisal.

A top ten list

Before installing electrochemical techniques at a plant, you should answer these questions:

1. *What is a suitable location to insert a probe?* Ideally the corrosion measurement should be made in an area where the corrosion processes will be most active, such that the worst case scenario is covered. Occasionally this may present some difficulties, particularly where the corrosion zone may fluctuate as a consequence of local conditions — for example, in condensing environments or oil/water mixtures. Sometimes corrosion modelling software can be used to

identify the most corrosive locations or to connect-the-dots between convenient monitoring locations. Installing the probe in a location where it is impossible to capture the process conditions that actually cause the corrosion renders any measurements useless.

2. *What type of probe should be used?* This depends on a number of factors. What will be the maximum operating temperature and pressure? Are the insulating materials suitable for the environment? Can a conventional off-the-shelf finger-style probe suffice or is a flush mounted probe or a flow-through probe more appropriate? Recent innovations with flange probes have made it possible to make almost any flange location a monitoring point. What exposed surface area of the material should be used? This directly impacts the sensitivity of the measurement techniques — lower corrosion rates require larger surface areas exposed. Are there special temperature-control requirements as in dew-point situations? Also, consider the expected probe lifetime and the complexity of the design of the probe. (The more robust solutions usually are the simplest.) There has been a good deal of experience for specific probe configurations in a variety of aqueous, multiphase and vapor applications.

The corrosion probe design is all important to the system as this is the component (sensor) that interfaces directly with the process environment. All too often, the quality and relevance of the corrosion data measured can be severely compromised by inappropriate probe design and electrode material selection.

3. *What is the most appropriate automated monitoring technique?* Is there a requirement for quick response? Is localized corrosion an issue? Can the measurement be made autonomously on a regular basis without operator control? Fortunately, electrochemical techniques can provide a measurement within a period of minutes; so the issue really becomes one of quality of data. Automated equipment such as SmartCET can now integrate multiple electrochemical techniques into a remote device that can be easily distributed at a reasonable cost per point.

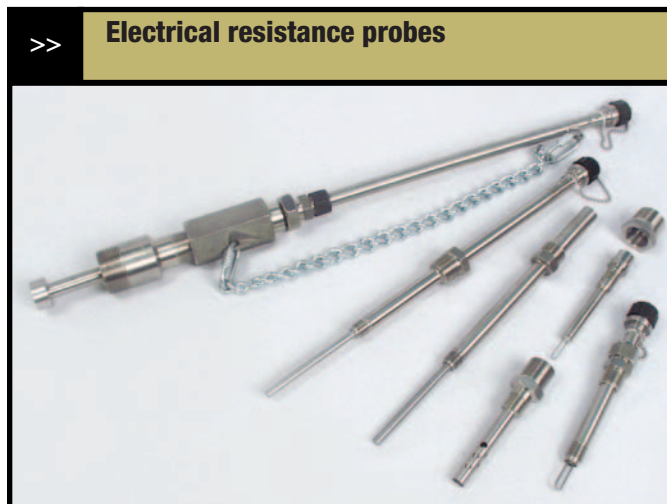


Figure 2. As the probe element corrodes, its electrical resistance changes, providing an indication of metal loss.

Source: Metal Samples

LPR, at first sight, is probably the easiest to implement but needs some methodology for minimizing the effects of noise in the corrosion process. Its application also requires some default value of the Stern-Geary constant.

HDA is field proven and has the advantages of allowing direct determination of the Stern-Geary constant and accurate corrosion rate.

EIS is not field proven and it can be difficult to automate interpretation and subsequent corrosion rate evaluation; a scan can take several hours to complete.

ECN, which is field proven, is the only choice if detection of localized corrosion is an issue.



Instantaneous corrosion monitoring



Figure 3. The SmartCET instrument, such as this one installed at a chemical plant, uses a number of electrochemical techniques for monitoring. Corrosion probes are a flow-through design installed via standard ANSI flanges.

Monitoring of some forms of localized corrosion, e.g., stress corrosion cracking, benefits from a probe configuration that reflects the physical attributes of the equipment being monitored; it may make sense, for example, to apply stress or put an artificial crevice on the working electrode. Also, it is important to note that some forms of corrosion such as erosion and cavitation are physical phenomena, although their *effects* can be detected electrochemically.

4. *How is data integrity assured?* Integrating automated system checks, fault detection and calibration, where necessary, is crucial.

5. *What is the response or cycle time of the measurement?* The measurement and analysis timeframe determines the data update rate to the distributed control system (DCS). Ideally this should be comparable to that for other inputs such as temperature, pressure, flow, etc., so that the corrosion information may be correlated with process operations.

6. *Can the instrument provide accurate general-corrosion-rate information?* Does it effectively deal with noise such as that caused by mains-voltage power lines? Does it incorporate a measurement of the Stern-Geary constant for determination of quantitative corrosion rates?

7. *What information can it supply about localized corrosion probability, i.e., Pitting Factor?* It is important to be aware of the transitions from general to localized corrosion as these can occur rapidly with changes in process conditions, quickly producing significant damage.

8. *How automated is measurement and analysis?* One of the major difficulties with migrating corrosion measurement techniques from the laboratory to the field is in automating the measurement and analysis routines. Embedded processors and sophisticated algorithms residing in firmware now can handle these issues.

9. *What does installation involve?* Installing the instrument should require minimum effort in terms of its location, wiring, set-up and training.

10. *How does the instrument interface with the DCS system?*

Ideally the DCS should allow an operator to view corrosion information as just another process variable. Corrosion data should be integrated with the DCS and plant historian to make it easier for analysis against other process data to identify interactions and the root causes of corrosion. This then gives the operator the possibility of mitigating or avoiding the corrosion by implementing the appropriate process controls or intervention with chemical mitigation, e.g., inhibitors and neutralizers.

The key to a successful system integration is in providing a simple data set to operators with a more robust set retained and channelled to process and corrosion specialists.

Real real-time value

A key objective for any corrosion management or mitigation program is to detect and resolve corrosion problems before significant equipment damage occurs. Today, newer field-proven methods can make that a reality at many chemical plants. These newer technologies, e.g., SmartCET, utilize on-line, real-time electrochemical corrosion monitoring to help correlate corrosion with processes and plant operations.

The technology works as well in primarily organic process streams with low water content and vapor phase conditions as it does in the more conventionally monitored aqueous streams, although probe design and use of Stern-Geary constants are keys to successful monitoring under these conditions.

By integrating on-line monitoring with process information management systems, operators and engineers can view in real-time corrosion data along with the other important process parameters like flow rates, temperatures, pressures and liquid levels. The real value proposition lies in achieving process optimization by keeping corrosion to a minimum while maximizing equipment uptime, production rates, product yield and plant safety. **CP**

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