White Paper

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Performance Improvement for Cooling Water Systems

Dawn C Eden, David A Eden, David Delve
Honeywell Process Solutions
Houston, TX, USA

Ayman Mehdawe
Honeywell Process Solutions
Abu Dhabi, U.A.E

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Abstract

Availability of cooling water system is critical to the operation of plant. Under inadequate control, the cooling water system can present significant difficulty to the plant in loss of production capacity, increased cost of cleaning and protective chemicals, increased energy and maintenance costs, and a reduction in service life. Although regular checks are made to determine water quality and compliance with prescribed operating conditions, these checks can be infrequent enough to allow corrosion, fouling and scaling to get out of control. This inevitably leads to outages that can be costly and severely affect production. Technology exists that enables a continuous, rapid update of the key general and localized (pitting) corrosion, scaling and fouling information that can assist the plant operator *in real-time* to ensure cooling water system availability.

This paper provides a latest update on a field proven on-line, real-time process control technology based on corrosion measurement that provides a comprehensive understanding of unit operating condition and fouling/scaling activity in cooling water and process water systems. Data from field-installed systems are presented. Recent advances in the technology and its implementation are also discussed, specifically with regard to wireless communications and direct-to-DCS capability.

Keywords: *Corrosion; pitting; under-deposit corrosion; fouling; scaling; cooling water; process water; materials selection, process control; wireless; DCS.*

Introduction

Failure of cooling water systems can lead to severe implications such as plant shutdown and even safety related incidents. Monitoring is an integral part of any industrial water treatment program. It is used to determine treatment effectiveness and to establish the optimum level of treatment that is most cost effective.

The purpose of corrosion monitoring is to assess or predict corrosion behavior of the system. Basically, there are two objectives to monitoring:

(1) To obtain information on the condition of the operational equipment and
(2) To relate this information to the operating variables (i.e., pH, temperature, water quality, chemical treatment).

Meeting these objectives will provide the following results:

1. Increase life of the plant
2. Improve the quality of the plant’s product
3. Predict maintenance needs at the plant
4. Reduce plant’s operating cost

Corrosion monitoring is standard practice in the industry. The plant engineer can use this information to predict equipment life. Monitoring helps the engineer identify significant factors responsible for corrosion problems and assures implementation of solutions.

Corrosion monitoring is a diagnostic tool. It provides information for the solution of corrosion problems. Knowledge of corrosion trends can be very valuable.

Frequently, several variables might appear to be significant, and the ability to correlate corrosion rates with a single variable under specific conditions can be vital. As a logical extension of its diagnostic capabilities, corrosion monitoring is used to assess the effectiveness of a solution to a specific water treatment problem.

Corrosion monitoring can be used to provide operational information. If corrosion can be controlled by maintaining a single variable (i.e., temperature, pH, chemical treatment) within limits previously determined, then that variable can be used to predict changes in corrosion patterns as the limits are exceeded in both a positive and negative direction.

An extension of this technique is to use a monitored variable to control chemical addition directly through automatic feed systems.

Causes of Corrosion

There are a number of variables which can influence corrosion rates, especially for mild steel water systems. The following list provides some of the key variables which can influence mild steel corrosion rates and their relative influence on corrosion:

1. Water Quality.
2. Temperature.
3. pH.
4. Water Velocity.
5. Oxidant.
6. Biomass or Slime.
7. Chloride and Sulfates.
8. Calcium Hardness.
9. Metallurgy.
10. Corrosion Inhibitors.

Corrosion Measurement and Control

The control and measurement of corrosion requires the correct identification of corrosion mechanism to enable optimized corrosion protection; specifically, the ability to differentiate between general and localized corrosion is critical. Pitting corrosion is most routinely assessed using long-term exposure of weight loss coupons as the identification of pitting via non-intrusive techniques has previously not been readily available. Most monitoring devices that can measure real-time corrosion rates, such as Linear Polarization Resistance (LPR) methods[1], can only detect general corrosion. As general corrosion is not the main cause of failure in most systems, especially where fouling and scaling can be expected to occur, this can lead to a false sense of security regarding the integrity of systems. Therefore, it is important that methods of detection of corrosion should address the forms of corrosion and methods of corrosion management.

It is well known and documented that coupons[2] can be analyzed to establish long-term localized corrosion rates as well as general corrosion rates, but this method of detection gives historic, retrospective information and not ‘real-time’ rates. If a reliable method of localized corrosion detection can be used, this will lead to a more confident prediction on the integrity of the system under study. This application can also be used to determine the effectiveness of the corrosion control methods, such as inhibitor programs.

Other monitoring methods, such as Electrical Resistance (ER) and Linear Polarization Resistance (LPR), can be used to provide more rapid information but these techniques are only capable of providing information regarding general or uniform corrosion. In circumstances where localized corrosion is the cause of failure, these methods have been found to give misleading information and can sometimes lead to no corrosion mitigation methods being deployed where they should have been. This can lead to failures where they are not expected.

The technology approach discussed in this paper employs a combination of Electrochemical Noise (ECN), Linear Polarization Resistance (LPR) and Harmonic Distortion Analysis (HDA) to provide output of a general corrosion rate, also a simple evaluation of how localized is the corrosion behavior (known as the Pitting Factor). The multi-technique monitoring system has been used to evaluate the mode of corrosion failure in cooling water and process water systems, and then subsequently employed in the same systems to help identify a suitable formulation and dosage level of corrosion inhibitor to control the localized corrosion.

Technology Overview

The measurement technology described in this paper is incorporated within the field proven on-line, real-time SmartCET® corrosion measurement transmitter (Figure 1) with on-board data manipulation capability to deliver trendable corrosion data to the distributed control system (DCS) for operator use. Plant support personnel, such as chemists and corrosion/reliability engineers, can also access on-line data (e.g. corrosion, process) together with off-line data (e.g. analytical, sample chemistry) via the plant’s data historian, enabling correlation and determination of ‘cause and effect’ scenarios.

Figure 1: Corrosion Transmitter and Example Probes

The standard corrosion transmitter can be connected to a variety of probes or sensors, each designed with an optimal electrode configuration to enable accurate corrosion measurement in small or large diameter equipment, high or low electrical conductivity, and in processes with a broad range of physical and chemical attributes.

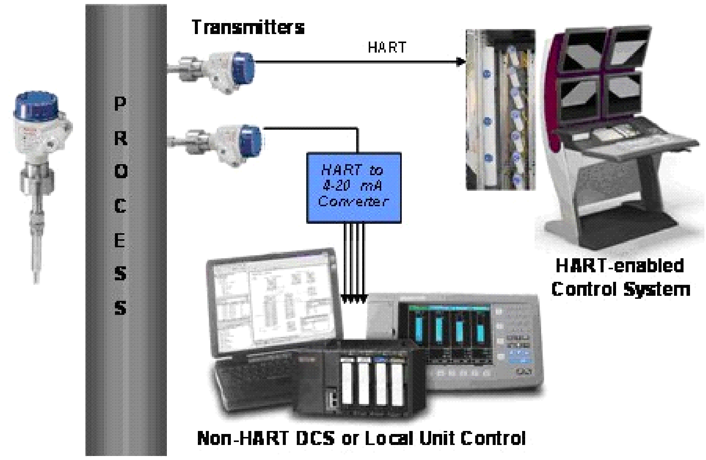

Figure 2: Data Connectivity on Plant

The transmitter is a loop-powered device that uses digital HART communications; 4-20mA analog data output is provided through use of a simple communications conversion device (HART interface module). The data can be output directly to a variety of end-user devices including distributed control systems (DCS), SCADA, paperless data recorders, etc. as depicted in Figure 2; data evaluation can be performed via the plant data historian in exactly the same manner as data treatment for pressure, temperature, flow and other typical process data points. By providing pre-calculated, trendable corrosion data directly at the plant user interface, the data can be both accessed and acted upon by the materials and reliability specialist, operations personnel or even utilized for automated chemical treatment control by way of an advanced process solution. Connection between the transmitter and the end-user device has traditionally been achieved through hardwire connection, such as 4-20mA current loop; however, the latest trends in transmitter and communications technology have enabled wireless communications that provide simpler implementation often at a lower installed cost. In this way, transmitters can be installed in locations that may have been precluded on the grounds of difficulty in cabling connection or cost of installation.

For more proactive real-time data that incorporates analytical measurements and enables progression to automated on-line control of water quality, an integrated approach may be taken as indicated in Figure 3. The corrosion measurement combines three individual electrochemical measurement techniques to provide the most accurate general corrosion rate as well as indications of a) localized (e.g. pitting) corrosion, and b) the tendency toward scaling (both non-conductive scales and the conductive iron sulfide that may result from microbiological activity).

From the instrumentation standpoint, the 4-20mA loop is usually configured to follow the general corrosion rate, which is often the single most important piece of information. The additional corrosion information may be accessed using digital HART protocol, the three additional variables being the Pitting Factor, B value and Corrosion Mechanism Indicator (CMI).

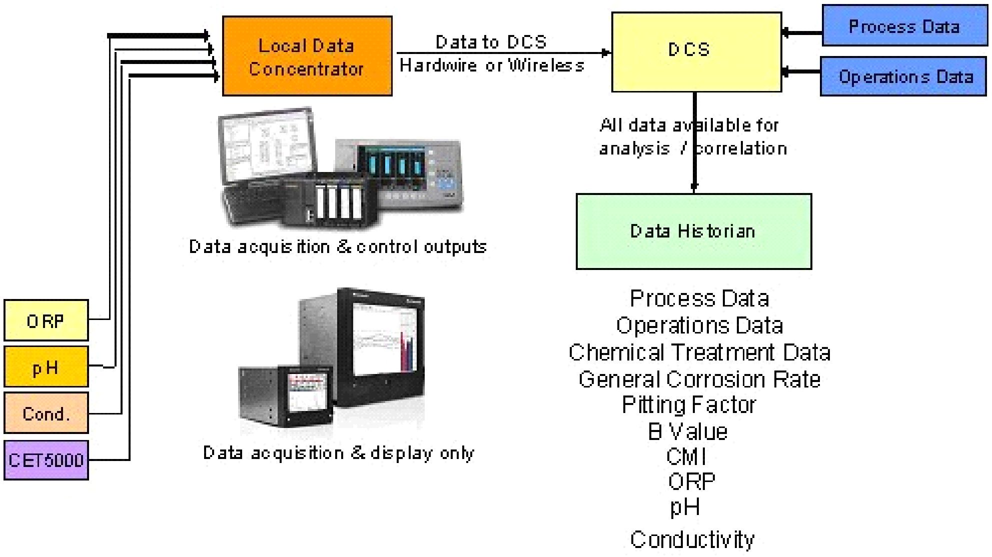

Figure 3: Integrated Approach; Enables Proactive Control, Automation

The reason why electrochemical techniques are used is due to the sensitivity and speed of measurement that enable correlation of changes in corrosion behaviour (either rate or mechanism) with even small, short-term variations in the process and corrosion control. Examples in a water system may be the impact of a loss of chemical delivery or even the ingress of oxygen into the system caused by the temporary opening of a valve.

Real-Time Multi-Technique Electrochemical Corrosion Measurement

The corrosion transmitter applies an automated data acquisition sequence that has been developed based on more than twenty years of experience in field corrosion measurement. Three electrochemical corrosion measurement techniques are used, providing parameters that describe the rate and the mode or mechanism of the corrosion processes. This technology provides the opportunity to assess both general and localized corrosion in a real operating environment.[3-8]

Linear Polarization Resistance (LPR): This technique has been in use for general corrosion measurement in field and laboratory applications since the 1960's. The methodology used in the on-line multi-technique instrument used in this study is a variation on this technique (a low frequency impedance), yet is able to utilize the same data treatment methodology. The technique applies a small potential perturbation to the working electrode, measuring the current response and hence generating a resistance value (the polarization resistance, R_p) which can be used to calculate a general corrosion rate.

$$i_{corr} = B/R_p, \qquad (1)$$

where B is the Stern-Geary 'constant' (mV),
i_{corr} is corrosion current density (mA/cm^2)

the Corrosion Rate (CR) then being developed through the relationship:

$$\text{CR in mmpy} = \frac{I_{corr} \text{ x seconds per year x atomic mass (g) x 10}}{\text{No. of electrons transferred x Faraday's constant x density (g cm}^{-3}\text{)}} \qquad (2)$$

The principle of the technique has a basis only in assessment of steady-state ‘uniform’ or ‘general’ corrosion, and so cannot be applied directly to studies of localized corrosion. In addition, a corrosion constant (known as the 'Stern-Geary constant' or 'B value') is an essential part of the corrosion rate calculation having a directly proportional relationship with the corrosion rate value. The B value is generally taken to be in the range 26-30mV for most metal/environment systems and is regarded by most suppliers of LPR instrumentation to be an instrument constant that is configured into an instrument at the factory. The B value is, however, not a constant value for all systems and can vary even within a system subject to changes, e.g. changes in temperature, flow, chemistry in the case of chemical processes and chemical treatment, and so on. Therefore, for accurate corrosion rate measurements, a variable B value should be used.

In the on-line, real-time, multi technique instrument LPR is used in conjunction with the second technique (Harmonic Distortion Analysis) during a data measurement cycle, where the latter technique is used to determine the B value.

Harmonic Distortion Analysis (HDA): This technique is an extension of the analysis of data obtained from the low frequency impedance measurement. The current response to a low frequency voltage sine wave is distorted due to the non-linearities of the charge transfer processes; this distortion is analyzed in terms of the fundamental response and the higher harmonics, to provide values for the corrosion current, the characteristic anodic and cathodic coefficients (Tafel slopes), and hence a value for the Stern-Geary constant. The subject instrument provides an output of the B value directly. The usual manner of treating the corrosion rate data is to analyze with time for an average B value, then post-correct the general corrosion rate. With experience of a particular system, the corrected B value can be input to the system settings (via the system software) to help provide the more accurate general corrosion rate as an on-line, real-time trend. The third method used by the on-line instrument is Electrochemical Noise.

Electrochemical Noise (ECN): Electrochemical Noise (ECN) is used to assess the localized nature of the corrosion process.[6] With ECN, no perturbation is applied to the probe electrodes; rather, the natural fluctuations in current and potential as the material corrodes are recorded. The ECN data is used primarily to produce a simple data output representative of how localized the corrosion is - the Pitting Factor (PF). The PF value is calculated according to:

$$PF = \sigma I / Icorr \qquad (3)$$

where

σI is the current recorded from ECN (mA)
I_{corr} is the corrosion current recorded by LPR (mA)

It is only possible to use this Pitting Factor relationship when the LPR and ECN measurements are made on the same three electrodes, as is the case with the described corrosion transmitter.

The PF value is viewed within the system software as a logarithmic value between 0.001 and 1, where,

a) PF < 0.01 (i.e. σ I is 1% or less of I_{corr}) represents general corrosion (a green alert zone)

b) PF in the range 0.01 to 0.1 (i.e. σ I is 1% to 10% of I_{corr}) represents an intermediate zone but still predominantly general corrosion (an amber alert zone)

c) PF > 0.1 (i.e. σ I is 10% to 100% of I_{corr}) represents localized corrosion (a red alert zone)

Measurement Cycle: The corrosion measurement is continuous and the each measurement cycle takes a period of 430 seconds.

Accurate General Corrosion Rate Measurement: As described above, the HDA data treatment enables the actual B value to be measured on-line, real-time enabling the most accurate calculation of corrosion rate possible. User experience has confirmed that a good agreement exists between the B value corrected corrosion rate and other corrosion assessment methods (e.g. weight-loss coupon exposure, ultrasonic thickness measurements).[9]

Optimizing Data Quality: The use of three complementary techniques helps to provide the most accurate corrosion rate estimate, an indication of how localized the corrosion is, also an assessment of corrosion mechanism as influenced by, for example, the presence of scales or films, or the loss of passivity or protection of the metal surface. The four corrosion data values help to characterize the corroding metal interface in terms of rate, mechanism (general or localized) and to detect the presence of species at the metal-solution interface (e.g. adherent non-conductive scales, electrically conductive films, adsorbed species).

Case Study 1

This first case study relates to an application where the user had a short-term need to assess the effectiveness of an existing chemical treatment program. In the course of measuring the corrosion behavior, the cooling water system was subject to a transition in the chemical treatment. Relating events to Figure 4, at time (1), the inhibitor was turned off, acid addition was stopped, blowdown was increased and a dispersant was added. A low pH event caused an increase in the corrosion rate and a change in corrosion mechanism. Within 24 hours, pit initiation and propagation were indicated. At time (2) it is observed that, although inhibitor injection was re-started, complete passivation was not achieved. A short-term reduction in localized corrosion activity was observed, but this increased again shortly afterward. Two weeks following the low pH event, significant localized corrosion activity was still indicated at time (3). In this case, the user was unable to achieve system control due to the off-line nature of the corrosion data evaluation, and the fact that the chemical treatment delivery system was operating entirely independently of any performance measurement. Had the chemical transition and its effects been identified on-line and in real-time such that the failure in chemical performance could be quickly recovered, the pitting corrosion could have been recognized and mitigated on a shorter timescale to enable its control through modified chemical treatment. This type of automated chemical delivery system is achievable through incorporation of the on-line corrosion information within an advanced control solution.

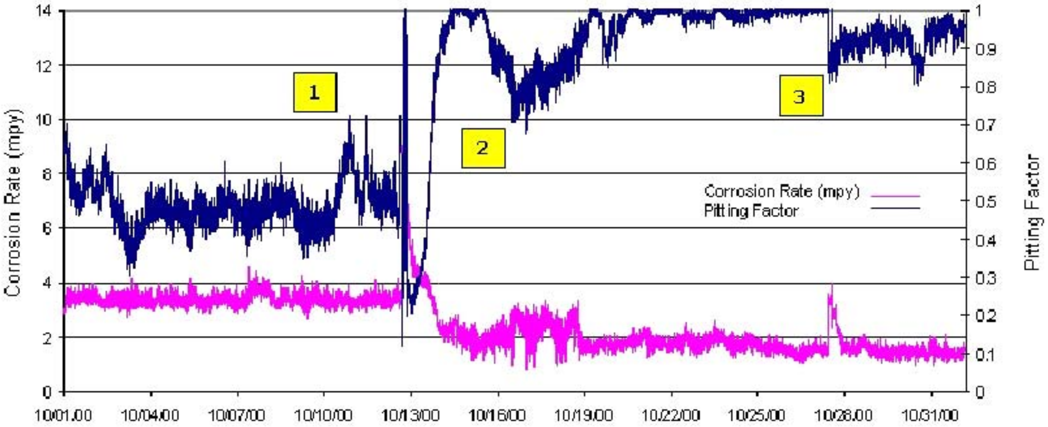

Figure 4: Case Study 1 - Corrosion Rate and Pitting Factor data with chemical treatment changes

Case Study 2

A second example involves a process water system that required investigation into the chemical treatment system, in particular the evaluation of inhibitor formulation to enable control of pitting corrosion.[10] Initially, coupons were used to determine the corrosive nature of the water system and indicated uninhibited corrosion rates of up to 60mpy. Following introduction of a corrosion inhibitor treatment, the general corrosion rate was shown by LPR to have reduced to below 1mpy; however, the weight loss coupons indicated that pitting had not been controlled. Accordingly, four inhibitors with different formulations were then tested.

To determine the corrosion rates in an untreated system, a test was run with the chemical turned off; after two days, product A was injected at 20 ppm to confirm the inhibited corrosion behavior. The results for this test are shown in Figure 5. The corrosion rate was around 0.2mpy which is low enough to determine that control of general corrosion had been achieved; however, the Pitting Factor was at a value of 1 and above, indicating the occurrence of pitting in the system.

In a subsequent comparative study, four products (A to D) were injected one after another to see how the instrument responded to the changes in inhibitor. The results from this study are shown in Figure 6 and are summarized below in Table 1.

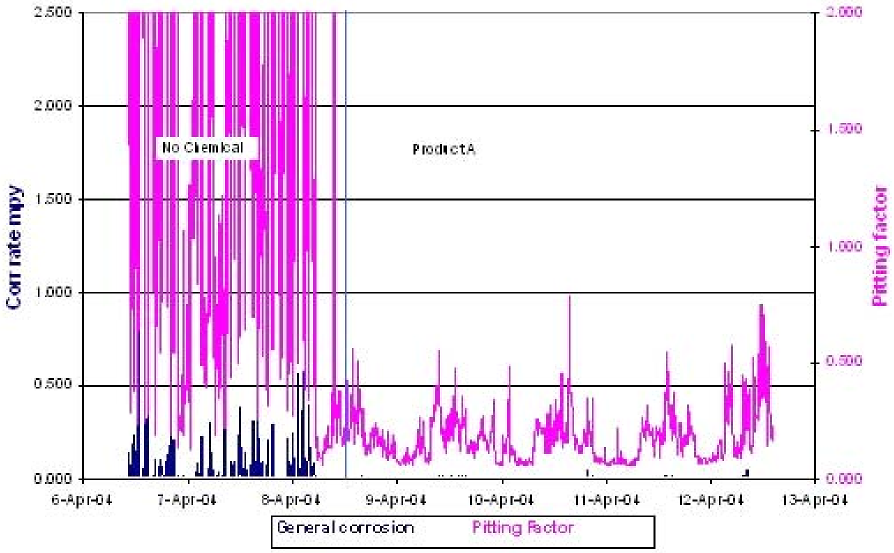

Figure 5: Case Study 2 - Initial tests showing corrosion rate and Pitting Factor results for inhibitor product A at 20 ppm

Product	Average Corrosion Rate (mpy)	Average Pitting Factor	Comments
Product A	0.02	0.25	
Product B	0.05	>2	Pitting Factor very high (>1)
Product C	0.03	1.8	Pitting Factor occasionally very high
Product D	0.01	0.15	

Table 1. Corrosion Rate and Pitting Factor results.

From these data, the greatest difference in inhibitor performances is evidenced by the range of Pitting Factor values. The products can be ranked in order of Product D, Product A, Product C and Product B for performance in inhibiting localized corrosion, and in the same order for the reduction in corrosion rates. Interesting to note is that the corrosion rate values all averaged below 0.1 mpy so, if general corrosion rate were the only criterion studied, it would be assumed that the system was under control in the presence of any of the inhibitor formulations.

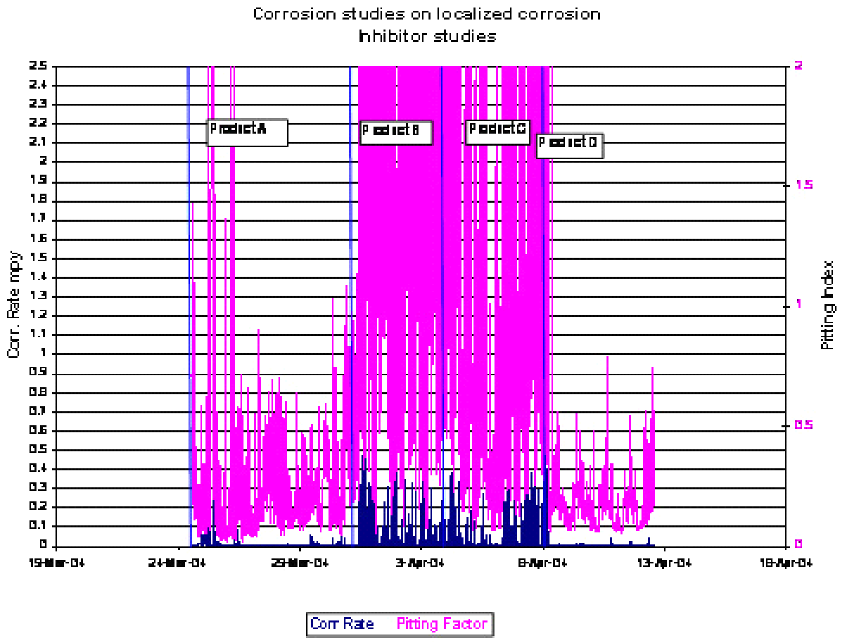

Figure 6: Case Study 2 - Tests showing results from four inhibitors (products A-D) tested in the water system.

As formulations of Product A and D only varied in the concentration of the components, and not in chemistry, it can be seen that the inhibitor composition can be optimized using this on-line, real-time approach. This approach allows the design of inhibitors to mitigate pitting as well as general corrosion and for the formulation to be finalized in the field where the real-life conditions are experienced. After these tests, Product D was commercialized for full field application and then deployed.

Improving Corrosion Control in Water Systems

For water systems, the corrosion and reliability teams are faced with a variety of issues related to materials (e.g. carbon steel, admiralty brass, stainless steel, etc.), water source (e.g. lakewater, river water, recycled water) and the need to operate the systems within the bounds of HS&E rules (e.g. for chlorination, chemical release, etc.). Corrosion losses and the detrimental effects of scaling and fouling can lead to costly materials upgrades to piping and condensers, often without operational knowledge of the likely performance or improved profitability to be expected. Similarly, the choice of chemical treatment and supplier may be made based upon the total contract cost rather than the actual performance delivered. The corrosion measurement discussed in this paper is applicable to all metallic materials in all electrically conductive water systems, and provides a cost-effective and simple means of determining materials selection for a given plant as well as proving the efficacy of the chemical treatment programs.

Advances in the automated, multi-technique corrosion monitoring system have made it possible to incorporate multiple corrosion measurements into a single instrument, significantly increase accuracy of the output data, and rapidly differentiate the onset of pitting from general corrosion as process conditions change. Further developments in the fields of transmitter and communications technologies have simplified the implementation of corrosion measurement and elevated it to the level of a true process variable.

Conclusions

General and pitting corrosion often provide the primary focus for chemical treatment programs in cooling water and process water systems, as most measurements that are provided by water system management tools are related to corrosion control. However, most measurements focus on “dosage” control of chemicals or symptomatic measurements of other parameters such as pH, iron counts, conductivity and ORP. Fouling also has a critical role in the optimized operation of cooling water systems but is rarely measured.

The corrosion monitoring technology that has been applied in the case studies is able to improve the operation of cooling water systems in the following ways:

- Optimization tool for chemical treatment programs
- Real-time problem solving tool
- Afford on-line materials evaluation and materials selection studies under actual service conditions
- With permanent implementation, provide a life-cycle performance monitoring tool for critical equipment
- Provide direct and immediate feedback to performance management and, through integration with automation and control systems, enable vastly improved chemical delivery

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Automation & Control Solutions
Process Solutions
Honeywell
2500 W. Union Hills Dr.
Phoenix, AZ 85027
Tel: +1-602-313-6665 or 877-466-3993
www.honeywell.com/ps

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