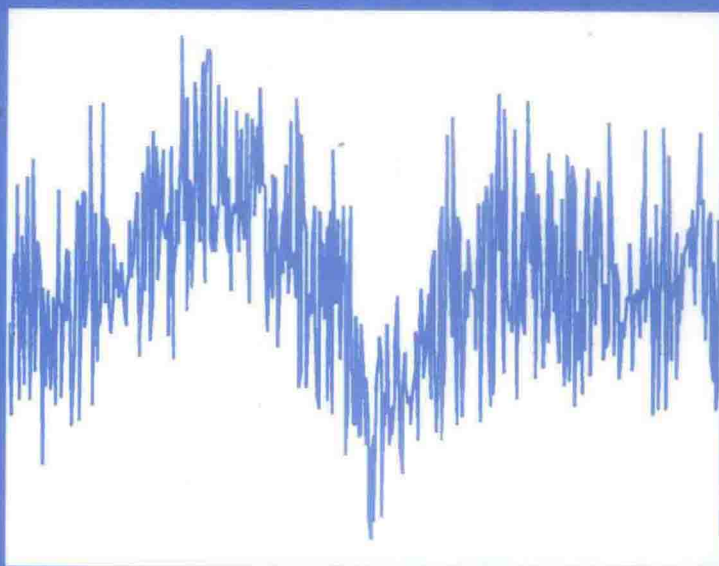


Electrochemical Noise Measurement *for Corrosion Applications*



*J. R. Kearns, J. R. Scully, P. R. Roberge,
D. L. Reichert, and J. L. Dawson, editors*



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*Jeffery R. Kearns, John R. Scully, Pierre R. Roberge,
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The quality of the papers in this publication reflects not only the obvious efforts of the authors and the technical editors, but also the work of these peer reviewers. The ASTM Committee on Publications acknowledges with appreciation their dedication and their contribution of time and effort on behalf of ASTM.

Foreword

This First International Symposium on Electrochemical Noise Measurement for Corrosion Applications was held in Montreal, Quebec, Canada on 15–16 May 1994. ASTM Committee G-1 on Corrosion of Metals sponsored the symposium. Jeffery R. Kearns, Alcoa Technical Center, Alcoa Center, PA, served as chairman of the symposium and was principal editor of this publication. John R. Scully, University of Virginia, Charlottesville, VA; Pierre R. Roberge, Royal Military College of Canada, Kingston, Ontario; David L. Reichert, DuPont Experimental Station, Wilmington, DE; and John L. Dawson, CAPCIS Ltd., Manchester, United Kingdom, served as symposium vice-chairmen and co-editors.

Overview

Electrochemical noise measurement (ENM) is a controversial subject. There are no established test methods, and there is no consensus on a theoretical framework for interpreting data. It is unusual for ASTM Committee G-1 on Corrosion, Deterioration, and Degradation of Materials to begin standards development under such circumstances. Nevertheless, a task group was formed by members that were both concerned about the rapidly growing commercial market for the technology and interested in pursuing fundamental work on a “new” electrochemical technique. The basic questions that ASTM Committee G-1 asks about any electrochemical technique that is proposed for standardization are “What does the proposed technique measure?,” “Have instruments and methods been established to make reliable measurements?,” and “Does the proposed technique provide useful information that is not possible to obtain by existing standardized techniques?” To answer these questions, the ASTM Committee G-1 Task Group on ENM and the symposium authors represented by this STP were charged with the task of developing consensus on three basic issues:

- (1) how should a measurement be made so that it can be compared with confidence to others,
- (2) what electronic measurement capabilities and calibration procedures are necessary to make a valid measurement, and
- (3) how can the data be most efficiently analyzed and reliably interpreted.

It is hoped that progress with these issues will lead to the creation of new corrosion test standards and the wider acceptance of the technique in research and industry.

Given the controversy surrounding the subject, it is appropriate to provide working definitions for the terms used in the title of this STP.

Electrochemical noise—Fluctuations of potential or current, typically of low frequency (<10 Hz) and low amplitude. Electrochemical noise originates, in part, from natural variations in electrochemical rate kinetics during a corrosion process. Electrochemical noise is often regarded as a random (stochastic) phenomena coupled to deterministic kinetics.

Electrochemical noise measurement—A technique involving the acquisition processing and analysis of electrochemical noise data. Data are typically acquired by monitoring the evolution of a corrosion process on two or more coupled electrodes without the application of an external signal. Alternatively, potentiostatic or galvanostatic methods can be used to measure electrochemical current or potential noise, respectively. Various electronic filtering and mathematical methods can be used to analyze electrochemical noise signals. With appropriate corroborating measurements and observations, ENM data can provide information concerning the nature of the corrosion process and the magnitude of the corrosion rate for a given system.

Historical Perspective

Fluctuations of the potential or current from a corroding electrode are a well-known and easily observable phenomenon. Before the 1970s, electrochemical noise was regarded as a source of bias and error that compromised electrochemical measurements rather than as a

rich source of information. (The reader is referred to the keynote address for a review of much of the early work on what is now considered to be ENM.) The use of electrochemical potential noise measurement (EPNM) as a corrosion research tool has increased steadily since Iverson's paper in 1968. The measurement of electrochemical current noise (ECN) between coupled electrodes combined with the measurement of EPNM was established as a viable industrial monitoring method by workers at the University of Manchester in the early 1980s. The use of the technology has grown in laboratories and industrial plants worldwide, such that by the end of the decade it was being called the "Technique of the Nineties."

ASTM Committee G-1 began to consider the development of standards on ENM in 1991 and formed a task group on the topic (J. R. Kearns, chair). The scope of the task group is to "develop standards that describe instruments and methods for making and analyzing electrochemical noise measurements." One of the first activities of the task group was to initiate the organization of an international conference on ENM to assess this technology and identify new areas for research and standardization.

Summary of the STP

This ASTM Special Technical Publication (STP) resulted from the first international symposium on Electrochemical Noise Measurement for Corrosion Applications held in Montreal, Quebec, Canada on 16 and 17 May 1994. Of the 36 presentations made at the symposium, 28 papers were approved (3 peers reviewed each paper) for this STP. The principal authors were from eight countries, including Canada (4), France (4), Mexico (3), New Zealand (1), Slovenia (1), South Africa (2), United Kingdom (3), and the United States (10) and represented a variety of industrial and academic perspectives on ENM. The papers have been grouped into six sections on Correlations to other Electrochemical Techniques, Data Analysis, Industrial Applications, Pitting, Methods, and Standardization. This STP provides a snapshot portrait of the state of the art for ENM in the early 1990s.

The fact that many of the papers in the STP, particularly in the Industrial Applications section, have one or more coauthors that are associated with the University of Manchester reflects the history of the commercial development of the technology at this institution. The reader should also note that an even greater number of papers in this STP are coauthored by individuals independent of the Manchester group. This fact not only serves to validate aspects of the early, industrially oriented work done in Manchester, but it also explains the rapid increase in the use of technology around the world during the past five years.

Overview of Papers

The keynote address (Dawson) is intended primarily to provide background for the non-specialist. Should the reader want more depth, an extensive list of references is included covering the scientific research leading to ENM, investigations of various forms of corrosion using ENM, and the application of ENM to industrial corrosion-monitoring situations. The title of the keynote address poses the question as to whether or not ENM is the definitive electrochemical technique. The answer to the question posed in the keynote title is **No!** ENM is not a panacea and is best used as one of several techniques in what is often referred to as a multitechnique approach. For this reason, the first section of this STP on Correlations to Other Electrochemical Techniques is very useful in establishing the validity of ENM and in demonstrating how it can be effectively combined with more established techniques.

Correlations to Other Electrochemical Techniques

Linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) are well-established corrosion measurement tools and are logical standards for qualifying ENM as a method for measuring general corrosion. In the first paper in this section (Bertocci) note that one must eliminate data from unwanted noise sources, and that trend removal may also be warranted. Whether using analog or digital (mathematical) filtering, caution must be exercised to prevent the elimination of valid data.

The next two papers (Mansfeld and Xiao and Reichert) found that the relatively new parameter unique to ENM called the noise resistance, R_n , correlated well with polarization resistance, R_p , as measured by ENM and LPR techniques, respectively. The manner in which R_n should be calculated was debated between the two papers ($R_n = V_n/I_n$ where V_n and I_n were taken as the root mean square [RMS] values of electrochemical potential noise and electrochemical current noise, respectively, in the first paper and as standard deviation values in the second paper). Selection of RMS or standard deviation values depends upon how the data were collected and filtered.

The second paper of the session (Mansfeld and Xiao) confirmed that frequency plots of ENM data are similar to EIS data and good agreement can be obtained between ENM and EIS data at the zero frequency limit. The authors prefer the EIS technique because it provides more information than ENM, especially for evaluating coated systems. It was observed in the Reichert paper that for very active systems (1.3 mm/y) the correlation of corrosion rate calculated from ENM did not correlate with that from R_p or mass loss data. The interpretation of the practical studies of uniform corrosion reported in this paper is regarded from a theoretical perspective in the first paper of the next session.

Data Analysis

The first paper of the section (Cottis et al.) addresses, in part, the need expressed in Reichert's paper for a theoretical basis relating ENM to corrosion rate. The authors conclude that the noise resistance parameter is a measure of essentially the same resistance as that obtained by conventional LPR methods. ENM is superior to LPR in measuring resistance in high-resistance systems.

The second paper (Kelly et al.) critically evaluates the correlation of two of the more common noise parameters, noise resistance and the pitting index, to conventional electrochemical and physical measures of degradation. The results, for AISI Type 410 stainless steel exposed to several test conditions that induce different modes and rates of corrosion, cast doubts on the credibility of these parameters for all systems. More work needs to be done to explain the apparent lack of correlation in the results of ENM and other methods for the alloy and environments in question.

A common way to analyze noise data in many science and engineering disciplines has been to transform time records to the frequency domain to obtain power spectra. Electrochemical noise signals often consist of a complex combination of deterministic and stochastic processes, so a common approach to analysis has been to correlate dominant frequencies and deconvolute unwanted signals in an iterative manner using established mathematical functions. For instance, power spectral density (PSD) plots are computed using algorithms such as the fast Fourier transforms (FFT) or the maximum entropy method (MEM). A comparison of these two methods is made in the third paper (Beaunier et al.) in which it was revealed that the validity of the low-frequency plateau obtained by the analysis of noise results with MEM can yield questionable results. The authors apply the technique to elucidate

a practical corrosion problem, the influence of molybdenum additions (in the case by implantation) to iron-chromium-nickel (Fe-Cr-Ni) alloys on pitting behavior.

The paradigm of nonlinear dynamics (also called chaos theory or fractals) is impacting everything from stock price forecasting to corrosion science. Analytical tools have been developed to detect and characterize deterministic or chaotic features in seemingly random data. The fourth and fifth papers of the session (Legat and Govekar and Roberge) review the jargon and some of the mathematics as would seem to be relevant to the analysis of ENM data. The techniques presented in both papers are illustrated by their use to reveal important features of complex ENM data. Legat and Govekar provide a general introduction to chaos and then demonstrate the utility of the techniques by identifying in experimental ENM data records changes in the mode of corrosion for a carbon and a stainless steel exposed to a changing test environment. Roberge describes and then applies two chaos techniques, the stochastic process detector and rescaled range analysis. The critical pH of a 5000 series aluminum alloy exposed to a series of salt solution of various degrees of acidity was identified by these techniques. Extensive lists of references for more in-depth knowledge in this important area are provided in both papers.

A quite different computer-based approach concludes the session (Barton et al.). Background to the technology is presented along with a case history that demonstrates the power of artificial neural networks to classify ENM data. In a case history, an artificial neural network is trained with many ENM time series records for AISI type 304 stainless steel in dilute chloride solution to identify the onset of localized corrosion.

Industrial Applications

The eight papers contained in this section survey the use of ENM in modern corrosion monitoring and in industrial service-relevant testing of materials. The goal of industrial corrosion monitoring is to provide a clearer picture of the conditions in an operating plant that lead to corrosion damage to avoid unscheduled downtime. The operating conditions resulting in corrosion are often transient and are frequently masked or by other events. Syrett and Cox present a modern approach to corrosion monitoring as realized through a series of programs sponsored by the Electric Power Research Institute (EPRI) over the past decade. This significant body of work demonstrates that corrosion monitoring by multiple techniques, including ENM, can be used as a sensitive indicator of the conditions within a system for purposes of corrosion prevention and process control.

In the second paper (Brennenstul et al.) of the section, ENM was successfully used to detect the effect that zebra mussel settlement has on the corrosion performance for stainless steel in comparison to steel. The exposure and monitoring was done at a field test site near the water inlet to Ontario Hydro's Nanticoke Thermal Generating Station. A number of parameters were monitored simultaneously, including coupling current, electrochemical current and potential noise, degree of localization, and noise resistance. ENM proved to be sensitive to changes associated with mollusk settlement, and collaborating evidence revealed that it was not detrimental to corrosion performance; in fact, the binding biopolymers were actually proposed to inhibit corrosion.

Nuclear wastes at the Savannah River site are partially processed and stored in plain carbon steel tanks. As described in the third paper of this session (Mickalonis et al.) based on the encouraging results of a preliminary laboratory study, Westinghouse decided to use an ENM-based monitoring system to assure that the corrosion inhibitors used to protect these tanks remained effective. Under inhibited storage conditions, the noise data was fairly stable. ENM was sensitive to the steel passive-active transition associated with greater solution nitrate

concentrations. The authors proposed that with appropriate calibration, the technique may also be useful for the detection of stress corrosion cracking (SCC).

Switching from the power industry, the next two papers in this section (DeBruyn et al. and Winters et al.) deal with the use of ENM for on-line monitoring in the oil and gas industries. At a Moss gas (Pty.) Ltd. (Republic of South Africa) gas plant in a pipeline downstream of reformer units, ENM was used to provide a continuous indication of the capacity of the service environment to support SCC and other types of localized corrosion. Conventional corrosion monitoring was ineffective for the condensing thin-film conditions in a wet CO-CO₂ gas service environment. A preliminary laboratory study was conducted to establish optimum probe and instrument configurations as well as measurement capabilities. Stressed and unstressed sensor probes were inserted directly into the process line. The ENM-based monitor was used to identify times when process conditions are such that the carbon steel pipeline may be susceptible to SCC. By instituting effective countermeasures at such times, there is the opportunity to prevent SCC of the pipeline by process control.

The second paper about monitoring in the oil and gas industries (Winters et al.) describes the development of a side-stream system that was designed to overcome many of the shortcomings of fouling monitors currently used in the treatment of cooling water. In addition to monitoring indicators of fouling, the system simultaneously monitors corrosion with ENM and two other supporting electrochemical techniques. A sensor array is integrated into the heat exchanger tubing bundle so that critical operating conditions can be monitored. In a field trial, the system was successfully used to verify the operating limits and scale deposit control capability of the water treatment packages.

The last three papers of the section (Macdonald et al., Brennenstuhl et al., and Doherty et al.) offer examples of how ENM can be used to evaluate materials of construction under test conditions relevant to the actual plant operating environment. The goal of the first service-relevant testing paper (Macdonald et al.) is to provide a clearer picture of the development of damage in a plant by measuring relevant parameters under actual operating conditions. The simplicity of the coupled electrode for monitoring electrochemical current noise provides for a sensor capable of monitoring changes in key parameters at elevated temperatures and pressures. The lack of such a sensor has impeded the introduction of monitoring systems for the thermal transport circuits of power plants. In quite a different test apparatus, ENM was explored as a means of detecting and monitoring stress corrosion cracking in sensitized Type 304 stainless steel in high-temperature water (up to 288°C). The magnitude and pattern of the data were used to detect changes in the chemical and physical properties of the fluid as well as the mode of corrosion.

The last two papers of the session (Brennenstuhl et al. and Doherty et al.), describe the use ENM in a multitechnique approach (ENM, open-circuit potential measurement, and zero resistance ammetry). From the data collected by the multitechnique approach, several ENM parameters were tracked versus time (for example, ECN standard deviation, mean coupling current, noise resistance, degree of localization, and pitting function) and related to subtle differences in the composition and microstructure of nickel base alloys as well as the simulated process environment. Workers at Ontario Hydro Technologies (Brennenstuhl et al.), suspected that differences in corrosion performance, as observed in-service, were masked in conventional testing by two factors: the aggressiveness of the test environment and the limited sensitivity of the corrosion measurement method. In the last paper of the session (Doherty et al.), workers from McDermott, Babcock, and Wilcox used ENM parameters to compare differences in simulated cleaning solution (NaOH) corrosivity, crevicing conditions, and composition on steam generator tubing performance. The noise resistance, degree of

localization, and standard deviation of ENM were found to be the most reliable parameters for making these three types of comparisons, respectively.

Pitting

The goal of the papers in this session is elucidate the mechanism of pitting through the sensitivity of the ENM technique. In the first paper of the session, Pride et al. measure EPN and ECN by galvanostatic and potentiostatic techniques, respectively, to examine the transition from metastable to stable pitting. High-purity aluminum, Al-Cu binary alloy, and AA 2024-T3 were examined under conditions of increasing applied potentials or chloride-ion concentration. ECN spikes were directly linked to individual metastable pitting events. Ratios of pit currents to pit radii at various growth times were analyzed. The formation of a stable pit was correlated to pit stabilization conditions producing ECN events that continuously exceeded the threshold ratio of 10^{-2} A/cm. This approach is promising since this ratio is fundamentally linked to the pit solution concentration required to maintain active pits.

In the second paper, Gorse et al. attempted to examine the effects of sulfur and titanium on the metastable pitting behavior of AISI 430 stainless steel by investigating the shapes of current transients. Individual ECN events associated with metastable pitting were described by current spikes which obeyed power law relationships. Attempts were made to relate the power law behavior of the current spike to the identity of the pit site, such as titanium carbide and manganese sulfide inclusions.

In the last paper of this session, Pistorius considers the merits of using either ECN or EPN to predict the transition from metastable to stable pitting in AISI 304 stainless steel. By coupling the stainless steel to a platinum cathode, it was shown that a large portion of the pit charge was supplied by capacitive currents from the adjacent platinum cathode. The size of potential fluctuations during metastable pit growth was argued to be related mainly to the pit charge (size) instead of pit current or current density. From prior work it was known that increasing pit currents for similarly sized pits provide a good indication of the transition to stable pitting. Therefore, EPN was viewed to have less merit as an indicator of pit stabilization than ECN. It was theorized that the standard deviation of metastable pit currents would provide a better indicator of the transition to stable pitting. However, the presence of heat tint oxides formed during heat treatment of samples complicated the establishment of straightforward relationships between ECN and conditions for pit stabilization for a variety of reasons.

Methods

In this section, ENM methods were applied to a diverse number of corrosion problems. In each paper, alternative corrosion monitoring tools augmented ENM studies. The first paper by Oltra et al. examined ECN and acoustic emission (AE) associated with the abrasive action of a slurry on a metallic target. The fluctuating AE and ECN signals were processed in two ways (statistical analysis of signals in the time domain and in terms of a spectral density plot) with the overall goal of quantifying the contributions to metal loss by mechanical wear and corrosion. A linear relationship was established between abrasive metal loss and the statistical analysis of acoustic signals. Interestingly, total corrosion currents could not be considered as the linear superposition of single current transients suggesting that the observed depassivation-repassivation events were not completely independent.

In the second paper, Huet et al. examined EPN associated with the proton discharge reaction both at open circuit and under applied cathodic polarization on iron using Devan-

athan permeation foils exposed to sulfuric acid. Simultaneously with EPN, associated fluctuations in electrolyte resistance on the charging surface and the hydrogen permeation flux on the exit surface of the foil were characterized. The hydrogen permeation flux is coupled to the behavior on charging surfaces through solid state hydrogen diffusion and fluctuations in charging surface lattice hydrogen concentrations could be estimated. These fluctuations were linked with hydrogen bubble formation and detachment from the charging surface under cathodic polarization. However, the origins of fluctuations for open circuit hydrogen production and ingress remained undetermined. Insight into factors affecting hydrogen absorption was gained.

In the third paper, Malo and Velazco sought to distinguish artificial noise signals associated with a rotating disk electrode device and other sources from noise of fundamental electrochemical origins. Artificial sources produced noise signals that did not exceed 10 μV and 0.1 μA . Corrosion processes for mild steel in Na_2SO_4 produced much larger noise levels in this system. In the next to last paper in the session, de Damborenea and Fernández examined ENM during the exfoliation corrosion of AA 8090 in the ASTM Test Method for Exfoliation Corrosion Susceptibility in 2XXX and 7XXX Series Aluminum Alloys (EXCO Test) (G 34). Power spectral density (PSD) and statistical methods, including noise resistances, were compared to charge transfer resistances obtained from EIS. The early stages of localized corrosion were detected by ENM, but strong correlations between ENM data and corrosion rates during severe exfoliation were generally lacking. EPN was used in the last paper of the session (Almeida et al.) to examine the protective nature of the corrosion products developed on pretreated and untreated carbon steels exposed at various Ibero-American atmospheric test sites. These samples were subsequently immersed in Na_2SO_4 solutions for linear polarization resistance (LPR) and EPN measurements at different times. Samples with higher corrosion rates, because of less protective oxide layers or more aggressive atmospheric conditions or both, correlated well with increased magnitudes of EPN particularly in the cases in which localized corrosion was promoted by chloride ion incorporation into oxide layers during exposure to marine atmospheres.

Standardization

The first paper by Bierwagen et al. covers several topics and is the only one in the STP with the goal of evaluating the reproducibility of data obtained for any given system. The authors present a significant body of data that should serve as a benchmark for future work in this area. By rigorously controlling test variables and statistically validating test results, the authors justify the use of ENM for the evaluated coated metal systems. The final paper (Kearns et al.) of the session and the symposium reviews the activities of the ASTM Committee G-1 task group on ENM since its beginning in 1991. The paper presents the group's first attempt to develop consensus on: (1) terminology, (2) specifications and configurations for laboratory instrumentation, (3) laboratory apparatus, and (4) data analysis methods. The proof of these deliberations is a test method and instrument specification that when followed yield a set of data for a given system that can be compared with confidence to others following the same. To this end, instrument specifications, test procedures, and test results are presented. It is hoped that this paper encourages participation in future task group activities and the round robin test program that is planned. An extensive list of terms related to ENM technology is defined in the Appendix to the paper, which the reader may find useful when reading this and other papers in this STP.

Current State and Future Directions

The reliable interpretation of ENM data is the major challenge to the advance of the technology in corrosion research, materials testing, and industrial monitoring. At this time, it has been established that ENM systems are capable of detecting subtle changes in the material or environment or both under a wide variety of plant processes and laboratory test conditions. With strong corroborating information from other sources, ENM data can be related with confidence to changes in corrosion behavior or environmental conditions or both. However, until a theoretical framework for interpreting corrosion events from ENM data are established and standardized testing practices are widely accepted, the reader is encouraged to be skeptical about detailed physical interpretations of ENM data in the absence of strong corroboration: As was stated at the symposium, "correlation alone is not sufficient to establish causality."

In addition to the reliable interpretation of data, other exciting developments are also anticipated. No doubt there will continue to be more unique applications for ENM in corrosion monitoring and even process control. The challenges encountered in the field will set the pace for much laboratory experimentation and research. In addition to successful industrial applications, the next major step toward validating ENM is anticipated to be in regard its use in elucidating various forms of localized corrosion, such as SCC and pitting. In addition to comparisons of parameters common to ENM and more established electrochemical techniques, such as LPR and EIS, one can also look forward to the analysis of ENMs by computer-intensive tools associated with artificial neural networks and nonlinear dynamics.

Measurement is the final area for future work that is anticipated based on a reading of this STP and discussions at the symposium. There is a need, in both the lab and plant, for techniques/instruments that can handle the large amounts of data that are acquired during real-time monitoring without losing valuable information. Specifically, more work is needed to define the best methods for electronic filtering, trend subtraction, and localized event recognition of ENM signals. However, in an era of incredibly powerful, inexpensive, user-friendly electronics and software, it is very important to consider just how electrochemical signals are processed into ENM data to avoid mis- and over-interpretation of data. With this caution in mind, it is essential that calibration procedures for instrumentation and reference-corroding systems be established along with diagnostic tests for the validity of data so that measurements can be compared with confidence. The ASTM Committee G-1 task group on ENM is an excellent forum to address these latter tasks.

Summary

The combined offerings of this STP provide the reader with a review of the state of the art of ENM in the early 1990s. The integration of ENM parameters with other electrochemical measures of system status demonstrate the optimum use of ENM technology. Many diverse industrial applications for ENM are presented along with the latest laboratory methods and data analysis techniques. The approaches of the individual groups varied according to the anticipated nature of the corrosive environment and the anticipated response of the material to it. In addition to material-environment considerations, the individual goals of the monitoring or testing operation also influenced decisions about what is to be measured and how data should be acquired and analyzed. Strategies to monitor and control corrosion in heat exchangers, pipelines, storage tanks, and steam generators using ENM technology are discussed from an industrial perspective. Workers from laboratories around the world are using ENM to glean new insights into traditional corrosion problems. From this plethora of

knowledge and experiences, a consensus is emerging on how to make ENMs, but the interpretation of ENM data and the optimum use of ENM technology for corrosion prevention and process control in industrial systems are issues that still present many challenges. It is hoped that some of the proposed test methods and data analysis techniques presented in this STP will gain wider acceptance and eventually lead to the development of new ASTM standards.

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